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by Frank J. Zeleznik and Sanford Gordon

Lewis Research Center
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TECHNICAL PAPER proposed for presentation at Fourth Annual
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ABSTRACT

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A comprehensive and balanced review of complex chemical equilibrium computations is given by considering not only some of the theoretical but also some of the pragmatic aspects of the problem. We begin by briefly surveying some of the pertinent thermodynamic principles and use these to derive and compare two alternate formulations of the equations governing chemical and phase equilibria. This is followed by a discussion of some algorithms for solving systems of nonlinear equations. We include not only a discussion of those algorithms which have been used in equilibrium computations but also some that have not been used but are potentially useful.

With this background, we present a historical review of some of the more significant developments in the calculation of complex equilibria. We conclude by giving examples of the application of thermodynamic computations to practical problems, and in this connection we point out how some common thermodynamic misconceptions can cause difficulties.

INTRODUCTION

Numerical calculations of chemical equilibria have concerned chemists and chemical engineers for a great many years; however, only rarely was it necessary for them to consider more than a single chemical reaction. Thus, to many individuals, chemical equilibrium was characterized by a single equilibrium constant and equilibrium compositions could be calculated almost triv-

ially. In a few situations, it was necessary to consider simultaneous equilibria involving perhaps two or three reactions. A relatively familiar case of such a situation is the successive ionization of polybasic acids such as the dibasic carbonic acid, H_2CO_3 or the tribasic phosphoric acid, H_3PO_4 .

As people began to study chemical processes at more extreme temperature and pressure conditions, it soon became apparent that they could no longer consider a small number of simultaneous equilibria. For example, to calculate the flame temperature for the combustion of a hydrocarbon in air it might be necessary to consider as many as 20 or more chemical reactions. As the number of reactions increased, so too did the mathematical difficulties. No longer could the simultaneous equilibrium constant relations be solved in closed form, even approximately. It became necessary to use either a trial and error, or an iterative approach to obtain solutions of the system of simultaneous equations.

Several different approaches have been used to obtain solutions of the system of simultaneous equations describing chemical equilibrium. Some of the calculational methods were designed for specific problems and often took advantage of some special characteristic of the particular problem to facilitate its solution. Other methods were intended to be multi-purpose schemes that could, at least in principle, be applied to any chemical equilibrium problem. Prior to the advent of computers the special purpose schemes were the most widely used. However, as computers became more generally available the tendency was to abandon the special methods in favor of the multi-purpose schemes.

At the present time a predominant proportion of the computations of chem-

ical equilibria are done with the multi-purpose schemes. Accordingly, we will emphasize these methods in our review and will go into a considerable amount of detail. On the other hand, only a cursory examination will be given to the special purpose schemes. We shall begin by briefly reviewing some of the thermodynamic principles and deriving the equations that are used in the computation of chemical equilibria. This will be followed by a presentation of some of the calculating techniques that are available for solving the nonlinear chemical equilibrium equations. Having established the necessary background, we will then be able to survey the literature and point out some of the advantages and disadvantages of the various equilibrium computation schemes that have been proposed. Finally we shall complete our paper by discussing the application of equilibrium computations to typical problems.

THERMODYNAMIC FUNDAMENTALS

Let us begin our considerations of chemical equilibria by giving a brief review of the pertinent thermodynamic fundamentals. This section will serve a dual purpose; it will act as a repository for some necessary formulae and also will introduce our notation. Those readers interested in a more detailed exposition of the subject should consult one of the several textbooks listed in the references 1 - 9. The excellent textbooks by Callen ¹, Kirkwood and Oppenheim ⁵ and Wilson ⁹ are particularly appropriate.

FUNDAMENTAL RELATIONS

Every thermodynamic system can be completely characterized by any one of its fundamental relations; that is, all the thermodynamic information about a system can be derived from it. The particular fundamental relation that is used is immaterial and is selected on the basis of convenience. For the in-

dependent variables temperature, T , and pressure, P , the appropriate fundamental relation is the one expressing the Gibbs free energy, G , in terms of T , P and the composition variables. All other thermodynamic quantities can be obtained from G and are expressed in these same variables. It should be noted that we will only consider pressure-volume work in our discussion. The function G is sometimes called a thermodynamic potential. If one wished to work instead with pressure and entropy, S , as the independent variables, then the fundamental relation would express the enthalpy H in terms of P , S and the composition variables. Since the temperature and pressure are convenient experimental variables, the Gibbs function is probably most familiar and will serve as the vehicle for our discussion. We will assume that several phases can exist in our system and that each chemical species is potentially present in each phase. We can then write our fundamental relation as

$$G = G(T, P, n_i^\alpha) \quad (\text{I. 1})$$

where n_i^α ($i = 1, 2, \dots, m$; $\alpha = 1, 2, \dots, p$) represents the number of moles of species i in the phase α . The Greek index on the mole numbers will label the phase while the Latin index will label the chemical species. Now the Gibbs free energy is an extensive property, proportional to the amount of material in the system. This implies that (I. 1) must be a homogeneous function of degree one in n_i^α .

$$G(T, P, \lambda n_i^\alpha) = \lambda G(T, P, n_i^\alpha) \quad (\text{I. 2})$$

From Euler's theorem on homogeneous functions we have immediately that

$$G = \sum_{i, \alpha} \mu_i^\alpha n_i^\alpha \quad (\text{I. 3})$$

where the chemical potential μ_i^α is defined to be

$$\frac{\partial G}{\partial n_i^\alpha} \equiv \mu_i^\alpha = \mu_i^\alpha(T, P, n_j^\beta) \quad (\text{I. 4})$$

and is homogeneous of degree zero in n_j^β ; that is, μ_i^α is an intensive quantity. A comparison of the differential of G , for fixed T and P , calculated from (I. 1) with that calculated from (I. 3) gives the well-known Gibbs-Duhem relationship⁵

$$\sum_{i, \alpha} n_i^\alpha d\mu_i^\alpha = 0 \quad (\text{I. 5})$$

THERMODYNAMIC EQUILIBRIUM

When the Gibbs function is used to describe the thermodynamic system, the condition for thermodynamic equilibrium has been stated in the following manner by Callen¹: "...the equilibrium state minimizes the Gibbs function over the manifold of states of constant temperature and pressure...". Thus at equilibrium G is an extremum and therefore the variation in G , produced by the independent variations, must vanish. Not all variations in the mole numbers n_i^α are independent. The variations δn_i^α must, as a minimum, satisfy the requirement that the total mass of each element is constant regardless of how element is distributed among the different chemical species in the system. This might be considered the least constrained problem. Additional types of constraints are possible. For example, an analogous but somewhat more constrained problem is obtained by requiring that the mass of each chemical species remains constant. Such a constraint is appropriate for the study of the distribution of chemical species among several phases. We will examine in some detail the mini-

mum constraint of conservation of the element. In order to formulate these constraints mathematically let $Z_i (i = 1, 2, \dots, l)$ be the symbol for the l elements that make up the thermodynamic system. These are distributed among the various species $Y_j^\alpha (i = 1, 2, \dots, m; \alpha = 1, 2, \dots, p)$. In this notation the chemical formula of a species can be written in the form

$$Y_j^\alpha = \prod_{i=1}^l (Z_i)_{a_{ij}} \quad (\text{I. 6})$$

The formula numbers a_{ij} represent the number of atoms of the i^{th} element in the j^{th} species. If the system contains $b_i^0 (i = 1, 2, \dots, l)$ gram-atoms of element Z_i then the conservation of the elements can be written as

$$\sum_{\alpha=1}^p \sum_{j=1}^m a_{ij} n_j^\alpha - b_i^0 = 0 \quad (i = 1, 2, \dots, l) \quad (\text{I. 7})$$

If ionization is considered, then the conservation of charge can be expressed in the same form as (I. 7) where charge is assumed to be the $(l + 1)^{\text{st}}$ "element". The value of b_{l+1}^0 is then zero and $a_{l+1,j}$ is the charge on the j^{th} species. Equation (I. 7) represents l constraints on the variations δn_j^α . These are supplemented by the non-negativity constraints $n_i^\alpha \geq 0$. There are only $(mp-l)$ independent variations because of the constraints (I. 7). However, all of the δn_j^α can be considered independently variable if we introduce l additional variables λ_i , the Lagrangian multipliers. Using Lagrangian multipliers $\lambda_i (i = 1, 2, \dots, l)$ the condition for equilibrium becomes

$$\delta \mathcal{G} = \sum_{j, \alpha} \left(\mu_j^\alpha + \sum_i \lambda_i a_{ij} \right) \delta n_j^\alpha + \sum_i \left(\sum_{j, \alpha} a_{ij} n_j^\alpha - b_i^0 \right) \delta \lambda_i = 0 \quad (\text{I. 8})$$

where

$$\mathcal{G} \equiv G + \sum_i \lambda_i \left(\sum_{j, \alpha} a_{ij} n_j^\alpha - b_i^0 \right)$$

Treating the variations of n_j^α and λ_i as independent not only gives

$$\mu_j^\alpha + \sum_i \lambda_i a_{ij} = 0 \quad (\text{I. 9})$$

but also (I. 7) since the use of the λ_i permitted us to regard all of the n_j^α as independently variable. We could, of course, have used any other set of independent variations expressible as a linear combination of the δn_j^α . The only effect of this change would be to replace (I. 9) by a new set of equations formed from a linear combination of the equations in (I. 9).

In any case, (I. 7) and either (I. 9) or some linear combination of the equations of (I. 9) represent a set of $(l + mp)$ nonlinear equations that must be solved to determine the equilibrium compositions and the Lagrangian multipliers. However (I. 9) is interesting from still another point of view. Notice that the term involving the Lagrangian multipliers λ_i is independent of the phase index α . Thus it contains the conditions for phase equilibria; that is, the chemical potential of a species is the same in all phases. This is precisely the condition that leads to the well-known phase rule of thermodynamics (Kirkwood and Oppenheim⁵). Finally let us point out that although the λ_i were introduced as a mathematical device, they can be given a physical interpretation. Substituting (I. 9) into (I. 3) and using (I. 7) we immediately obtain

$$G = - \sum_i \lambda_i b_i^0 \quad (\text{I. 10})$$

Thus $-\lambda_i$ represents the contribution of the element Z_i to the Gibbs free energy of the system.

CHEMICAL REACTIONS

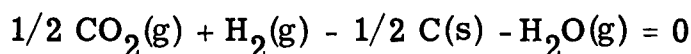
Since, in the above formulation, the δn_j^α could be regarded as independent variations only at the expense of introducing l new variables, λ_i , it would seem that this formulation is perhaps not the most economical. In chemical thermodynamics it has long been the practice to use independent variations corresponding to relatively simple processes that can be written in the form of chemical reactions. Thus, for example, we might write the reactions

$$\sum_{j, \alpha} A_{jr}^{\alpha} Y_j^{\alpha} = 0 \quad r = 1, 2, \dots, (mp - l) \quad (\text{I. 11})$$

Because of the one-to-one correspondence between the n_j^α and the Y_j^α the l relations (I. 7) among the n_j^α implies that we have l relations among the Y_j^α . Equivalently, this means that the matrix A_{jr}^{α} must be of rank $(mp - l)$. The A_{jr}^{α} are called the stoichiometric coefficients for the r th reaction and are chosen so that the elements are conserved in each of the reactions represented by (I. 11). This implies that the A_{jr}^{α} must satisfy the relations

$$\sum_{j, \alpha} a_{ij} A_{jr}^{\alpha} = 0 \quad (\text{I. 12})$$

Conventionally, the A_{jr}^{α} are taken to be positive for the products and negative for the reactants. A concrete example of (I. 11), for which the condition (I. 12) is satisfied, is the reaction



It should be pointed out that although the reactions (I. 11) may be significant kinetically, they are superfluous thermodynamically since all the compositions are already determined by (I. 7) and (I. 9). In a sense, these chemical reactions violate the spirit of thermodynamics since they specify a mechanism, or path, by which reactants are converted to products. As is well known, classical thermodynamics deals only with state functions and for any thermodynamic process it is only necessary to know the two end points of the process and not the detailed path connecting them. The reactions (I. 11) should most properly be regarded only as an artifice for introducing $(mp - l)$ independent variations, $\delta \xi_r$, one for each reaction.

In order to relate the variations δn_j^α to the $\delta \xi_r$, we proceed in the following manner. The change in the number of moles of Y_j^α produced by the r^{th} reaction can be written

$$(\delta n_j^\alpha)_r = A_{jr}^{\alpha \cdot} \delta \xi_r \quad (\text{I. 13})$$

The quantity ξ_r is called the extent of reaction for the r^{th} reaction and is defined by (I. 13). The total change in Y_j^α is then obtained by summing (I. 13) over all the reactions

$$\delta n_j^\alpha = \sum_r A_{jr}^{\alpha \cdot} \delta \xi_r \quad (\text{I. 14})$$

It is apparent from (I. 14) that we can replace the variations δn_j^α in equation (I. 8) with independent variations $\delta \xi_r$. As was pointed out, thermodynamically the chemical reactions are quite arbitrary and hence so too are the $A_{jr}^{\alpha \cdot}$ with only the requirement that its rank be $(mp - l)$. Now substituting (I. 14) into (I. 8) and rearranging we obtain

$$\delta \mathcal{G} = \sum_r \left[\sum_{j, \alpha} A_{jr}^{\alpha \cdot} \mu_j^\alpha + \sum_i \lambda_i \left(\sum_{j, \alpha} a_{ij} A_{jr}^{\alpha \cdot} \right) \right] \delta \xi_r + \sum_i \left(\sum_{k, \beta} a_{ik} n_k^\beta - b_i^0 \right) \delta \lambda_i = 0 \quad (\text{I. 15})$$

Using (I. 12) we find that the conditions of chemical equilibrium take the form

$$\sum_{j, \alpha} A_{jr}^{\alpha \cdot} \mu_j^\alpha = 0 \quad (\text{I. 16})$$

and also we again obtain (I. 7). Because of the use of independent variations the λ_i have disappeared from the problem. As a matter of fact we could have obtained this result directly from a variation of G without introducing the λ_i if we had regarded G as a function of ξ_r . Alternately, the direct elimination of λ_i from (I. 9) using (I. 12) also gives (I. 16). These equations represent the equilibrium constant expressions for the chemical reactions (I. 11). In this equilibrium constant formulation of chemical equilibrium the compositions are obtained by the simultaneous solutions of the set of (mp) nonlinear equations represented by (I. 7) and (I. 16). In passing we might point out that the expression on the left-hand side of (I. 16) is the negative of de Donders affinity for the r^{th} reaction⁹.

Since the two formulations of the equations governing chemical equilibrium, (I. 7, I. 9) and (I. 7, I. 16), have a common origin, their content is the same. The only difference at this point is that the former set involves (mp + l) equations while the latter involves only (mp) equations. This is somewhat compensated by the fact that in the second formulation one must determine a set of stoichiometric coefficients $A_{jr}^{\alpha \cdot}$. In a small system where the number of constituents (mp) is relatively small the determination of the $A_{jr}^{\alpha \cdot}$ usually presents no problem; however, when (mp) is large, it is important to have a more systematic procedure for determining the stoichiometric coefficients. Brinkley¹⁰

has discussed this problem in terms of the linear independence of a set of vectors constructed from the a_{ij} . With each species Y_j^α we can associate a column vector \underline{y}_j^α

$$Y_j^\alpha \longleftrightarrow (\underline{y}_j^\alpha)^T = (a_{1j}, a_{2j}, \dots, a_{lj}) \quad (\text{I. 17})$$

where the T on the column vector indicates the transpose. Not all of these vectors will be linearly independent and, in fact, only $c \leq l$ will be linearly independent. Generally, the equality holds and only in special situations does the inequality apply. We will henceforth assume $c = l$. Designating the linearly independent vectors by \underline{c}_i ($i = 1, \dots, l$) we can write

$$\underline{y}_j^\alpha - \sum_{k=1}^l c_k \nu_{kj} = 0 \quad (\text{I. 18})$$

The phase index does not appear on ν_{kj} since $\underline{y}_j^\alpha = \underline{y}_j^\beta$ and therefore the ν_{kj} must be independent of phase. Corresponding to the relationship (I. 18) we have the independent reactions (I. 11) written in the form

$$Y_j^\alpha - \sum_{k=1}^l C_k \nu_{kj} = 0 \quad (\text{I. 19})$$

where C_k represents the chemical formula of the species corresponding to the independent vectors \underline{c}_i . The C_k are called components and need not all be from the same phase. The ν_{kj} play the role of stoichiometric coefficients. When the indices α, j take the values corresponding to the components, the equations (I. 18) and (I. 19) are identically zero. The choice of components is not unique and from a theoretical point of view all choices are equally good. The chemical reactions (I. 19) can now be used to obtain a particular set of A_{jr}^α by comparison with (I. 11). Additionally the conservation of elements

can be written in terms of the ν_{kj} . Based on (I. 19) the analog to (I. 6) would be

$$Y_j^\alpha = \prod_{k=1}^l (C_k)^{\nu_{kj}} \quad (\text{I. 20})$$

The conservation of elements would now be written as a conservation of components

$$\sum_{j, \alpha} \nu_{kj} n_j^\alpha = q_k^0 \quad (k = 1, 2, \dots, l) \quad (\text{I. 21})$$

where the q_k^0 represents the moles of the component C_k that must be introduced into the system to achieve the overall composition. The numbers q_k^0 can be expressed in terms of the b_k^0 and the formula numbers, a_{ij} , of the components. The conservation relations in terms of components could be used in the minimization of free energy. However no particular advantage is gained since this merely replaces a_{ij} with ν_{ij} in (I. 9), causes $-\lambda_i$ be interpreted as the contribution of the i^{th} component to the Gibb's free energy, and replaces b_i^0 with q_i^0 in (I. 10). The conditions of chemical equilibrium (I. 16) corresponding to the reactions (I. 19), can be written in the dimensionless form

$$\frac{1}{RT} \left[\mu_j^\alpha - \sum_{k=1}^l \mu_k \nu_{kj} \right] = 0 \quad (\text{I. 22})$$

where the μ_k are the chemical potentials of the components.

The formulation of the equations for determining equilibrium compositions assumed that the thermodynamic state was specified by assigning the temperature and pressure. That is, in addition to either the set of equations ((I. 7), (I. 9)) or ((I. 7), (I. 16)) we had the pair of trivial equations

$$\begin{aligned} T &= T_0 \\ P &= P_0 \end{aligned} \tag{I. 23}$$

where T_0 , and P_0 are constants. However any two thermodynamic state functions could have been used for the same purpose. For example, to calculate the flame temperature for a constant pressure combustion (I. 23) would be replaced by

$$\begin{aligned} H(T, P, n_i^\alpha) &= H_0 \\ P &= P_0 \end{aligned} \tag{I. 24}$$

where H is the enthalpy and H_0 is a constant equal to the enthalpy of the reactants. For an isentropic or constant entropy process the state may be specified as

$$\begin{aligned} S(T, P, n_i^\alpha) &= S_0 \\ P &= P_0 \end{aligned} \tag{I. 25}$$

In general, we require any two equations involving T , P , and n_i^α to specify the state. The particular ones that are used are largely a matter of convenience.

Often chemical equilibrium problems occur that do not require the generality of the minimum constraint problem just discussed. Typical of such problems is the class of problems related to the distribution of chemical species among several phases. A simple and familiar example of such solvent extraction problems is the distribution of iodine between water and carbon tetrachloride. An example with physiological importance is the distribution of chemicals between the interior of the red blood cells and the blood plasma¹¹⁻¹².

Problems of this kind are all characterized by the fact that no "chemical reactions" take place; that is, the total amount of each species remains constant. Additionally, we may wish to take into account the existence of actual or imaginary semi-permeable membranes. Thus in our water-carbon tetrachloride-iodine example we can imagine the water phase to be separated from the carbon-tetrachloride phase by a membrane that is permeable only to iodine. This is a permissible assumption because of the small mutual solubility of water and carbon-tetrachloride. For the purpose of formulating the equilibrium equations let us suppose that each phase is surrounded by a semi-permeable membrane that is permeable to all species except the m^{th} . Then our constraining equations are

$$\sum_{\alpha=1}^p n_i^{\alpha} = b_i^0 \quad (i = 1, 2, \dots, m - 1)$$

$$n_m^{\alpha} = c_m^{\alpha} \quad (\alpha = 1, 2, \dots, p) \quad (\text{I. 26})$$

where b_i^0 now represents the total moles of the i^{th} species introduced into the system and c_m^{α} represents the number of moles of m^{th} species introduced into the α^{th} phase. Additional non-transferable species could be introduced without any essential complication. The chief difference between the reaction equilibria discussed previously and phase equilibria is the larger number of components or independent species. Each of the first $m - 1$ species is now a component while the m^{th} species furnishes p additional components. The condition for equilibrium now becomes

$$\delta \left[G + \sum_{i=1}^{m-1} \lambda_i \left(\sum_{\alpha=1}^p n_i^\alpha - b_i^0 \right) + \sum_{\alpha=1}^p \lambda_m^\alpha (n_m^\alpha - c_m^\alpha) \right] = \sum_{\alpha=1}^p \left[\sum_{i=1}^{m-1} (\mu_i^\alpha + \lambda_i) \delta n_i^\alpha + (\mu_m^\alpha + \lambda_m^\alpha) \delta n_m^\alpha \right] + \sum_{i=1}^{m-1} \left(\sum_{\alpha=1}^p n_i^\alpha - b_i^0 \right) \delta \lambda_i + \sum_{\alpha=1}^p (n_m^\alpha - c_m^\alpha) \delta \lambda_m^\alpha = 0$$

Therefore we obtain

$$\begin{aligned} \mu_i^\alpha + \lambda_i &= 0 \quad i = 1, 2, \dots, m-1; \alpha = 1, 2, \dots, p \\ \mu_m^\alpha + \lambda_m^\alpha &= 0 \quad \alpha = 1, 2, \dots, p \end{aligned} \tag{I. 27}$$

and in addition we also obtain the constraining equations (I. 26). The equations (I. 27), together with (I. 26), can be used to calculate the equilibrium compositions. It should be noted that here too the Lagrangian multipliers could be eliminated to reduce the number of equations and obtain the equations corresponding to the "equilibrium constant" formulation of the problem.

THERMODYNAMIC DERIVATIVES

Principally we have relied on the axioms of thermodynamics and our manipulations to this point have been quite general. There is still one more topic that we can discuss without introducing simplifying assumptions. In addition to the equilibrium compositions and the thermodynamic functions such as enthalpy and entropy one often would like to have the first derivatives of these functions. Fortunately it turns out that all first derivatives can be expressed in terms of three of them. For example, using the so-called Bridgman tables as tabulated by Glasstone⁴, all the derivatives can be expressed in terms of $C_P \equiv \partial H / \partial T$, $\partial V / \partial T$ and $\partial V / \partial P$. In comparison with the determination of

equilibrium compositions the evaluation of these three derivatives is almost trivial once the equilibrium compositions have been determined. The reason for this is that the calculation of these derivatives involves the solution of a set of linear equations whereas equilibrium compositions can only be obtained by solving a set of nonlinear equations. The enthalpy and volume of the system can be written as

$$H = G + TS = \left(1 - T \frac{\partial}{\partial T}\right) G = \sum_{i, \alpha} H_i^{\alpha} n_i^{\alpha} = \sum_{\alpha} H^{\alpha} \quad (\text{I. 28})$$

$$V = \frac{\partial G}{\partial P} = \sum_{i, \alpha} V_i^{\alpha} n_i^{\alpha} = \sum_{\alpha} V^{\alpha} \quad (\text{I. 29})$$

where $H_i^{\alpha} \equiv \partial H / \partial n_i^{\alpha}$ and $V_i^{\alpha} \equiv \partial V / \partial n_i^{\alpha}$ are the partial molar enthalpies and volumes respectively and where $H^{\alpha} = \sum_i H_i^{\alpha} n_i^{\alpha}$ and $V^{\alpha} = \sum_i V_i^{\alpha} n_i^{\alpha}$ are the enthalpy and volume of the α^{th} phase. Equation (I. 29) can be regarded as the equation of state for the system since it expresses the volume in terms of the temperature, pressure and composition. The differentiation of these expressions gives

$$C_P = \sum_{i, \alpha} C_i^{\alpha} n_i^{\alpha} + \sum_{i, \alpha} H_i^{\alpha} \frac{\partial n_i^{\alpha}}{\partial T} \quad (\text{I. 30})$$

$$\frac{\partial V}{\partial T} = \sum_{i, \alpha} \frac{\partial V_i^{\alpha}}{\partial T} n_i^{\alpha} + \sum_{i, \alpha} V_i^{\alpha} \frac{\partial n_i^{\alpha}}{\partial T} \quad (\text{I. 31})$$

$$\frac{\partial V}{\partial P} = \sum_{i, \alpha} \frac{\partial V_i^{\alpha}}{\partial P} n_i^{\alpha} + \sum_{i, \alpha} V_i^{\alpha} \frac{\partial n_i^{\alpha}}{\partial P} \quad (\text{I. 32})$$

where we used the fact that H_i^{α} and V_i^{α} are homogeneous of degree zero in

n_j^β . In each of these three expressions the second term represents the effect of composition changes produced by changes in the system temperature or pressure. To evaluate the three derivatives (I. 30), (I. 31), (I. 32) one must know $\partial n_i^\alpha / \partial T$ and $\partial n_i^\alpha / \partial P$. These can be obtained by solving the set of linear equations obtained by differentiation from either the set of equations ((I. 7), (I. 9)), or ((I. 7), (I. 16)) or perhaps the set ((I. 26), (I. 27)). Thus from the set ((I. 7), (I. 9)) we obtain for the temperature derivatives

$$\sum_{\beta, k} \mu_{j k}^{\alpha \beta} \frac{\partial n_k^\beta}{\partial T} + \sum_i \frac{\partial \lambda_i}{\partial T} a_{ij} = S_j^\alpha \quad (\text{I. 33})$$

$$\sum_{\beta, k} a_{ik} \frac{\partial n_k^\beta}{\partial T} = 0$$

where

$$\mu_{j k}^{\alpha \beta} = \mu_{k j}^{\beta \alpha} = \partial^2 G / \partial n_k^\beta \partial n_j^\alpha$$

and where

$$S_j^\alpha \equiv \partial S / \partial n_j^\alpha$$

is the partial molar entropy. Similarly the derivatives with respect to pressure are obtained by solving

$$\sum_{\beta, k} \mu_{j k}^{\alpha \beta} \frac{\partial n_k^\beta}{\partial P} + \sum_i \frac{\partial \lambda_i}{\partial P} a_{ij} = -V_j^\alpha \quad (\text{I. 34})$$

$$\sum_{\beta, k} a_{ik} \frac{\partial n_k^\beta}{\partial P} = 0$$

The Lagrangian multipliers λ_i were given a physical interpretation by (I. 10). An analogous interpretation can be given to their temperature and pressure derivatives. Recalling that μ_i^α is homogeneous of degree zero in n_j^β we have from Euler's theorem on homogeneous functions

$$\sum_{\alpha, j} n_j^\alpha \mu_j^{\alpha\beta} = 0 \quad (\text{I. 35})$$

This may be regarded as a variant of the Gibbs-Duhem relation (I. 5). Multiplying the first members of both (I. 33) and (I. 34) by n_j^α and summing over α, j gives

$$\sum_i \frac{\partial \lambda_i}{\partial T} b_i^0 = S \quad (\text{I. 36})$$

$$\sum_i \frac{\partial \lambda_i}{\partial P} b_i^0 = -V$$

Alternately these relations could have been obtained directly from (I. 10) by differentiation.

THE FORM OF THE GIBBS FREE ENERGY

Some pragmatic considerations permit us to make a considerable simplification not only in equations (I. 33) and (I. 34) that are used for calculating derivatives but also in all thermodynamic relations. To accomplish this simplification we will make our first, albeit very minor, assumption. We shall assume that each phase contributes additively to the Gibbs free energy or, equivalently, that we are neglecting all interactions among the phases

$$G = \sum_{\alpha} G^{\alpha}(T, P, n_i^{\alpha}) \quad (\text{I. 37})$$

This is a good assumption so long as the phases are not finely dispersed in one another. Henceforth all our calculations will be within the framework of the assumption (I. 37). This assumption makes the matrix $\mu_{jk}^{\alpha\beta}$ the direct sum of submatrices corresponding to each of the phases.

$$\mu_{jk}^{\alpha\beta} = \delta^{\alpha\beta} \mu_{jk}^{\beta\beta} \quad (\text{I. 38})$$

Some of our subsequent discussions will be facilitated if we have some idea of the structure of the chemical potential. Therefore, we will briefly look at the functional form of the chemical potential. A much more detailed presentation is available in the text by Kirkwood and Oppenheim⁵. The chemical potential for the i^{th} species in the α^{th} phase can generally be written in the form

$$\mu_i^\alpha = \bar{\mu}_i^\alpha + \Delta\mu_i^\alpha \quad (\text{I. 39})$$

where $\bar{\mu}_i^\alpha$ represents the contribution from ideal behavior and $\Delta\mu_i^\alpha$ represents the contribution from non-ideality. The quantity $\Delta\mu_i^\alpha$ is usually called the excess chemical potential and often must be obtained from experimental measurements^{2, 6-7}. In some cases it can be estimated theoretically as, for example, in the case of non-ideal gases obeying a virial equation of state¹³ or in the case of Debye-Huckel plasmas¹⁴. The ideal chemical potential, $\bar{\mu}_i^\alpha$, is characterized by an extremely simple concentration dependence, the logarithm of the mole fraction

$$\bar{\mu}_i^\alpha(n_j^\alpha, T, P) = {}^0\mu_i^\alpha(T, P) + RT \ln (n_i^\alpha/n^\alpha) \quad (\text{I. 40})$$

In this equation ${}^0\mu_i^\alpha$ is an arbitrarily selected reference value for the chemical

potential of the i^{th} species in the α^{th} phase; n^α represents the total number of moles in the α^{th} phase and is defined by

$$n^\alpha \equiv \sum_i n_i^\alpha \quad (\text{I. 41})$$

The reference values of the chemical potentials for the gaseous phase ($\alpha = 1$) are generally taken to be the chemical potentials of the pure species considered as ideal gases at a temperature T and a pressure P

$${}^0\mu_i^\alpha(T, P) = {}^*\mu_i^1(T) + RT \ln P \quad (\text{I. 42})$$

Here ${}^*\mu_i^1(T)$ is the ideal gas chemical potential of the i^{th} species at zero pressure. This is a convenient choice since ${}^*\mu_i^1$ can be calculated from spectroscopic constants by evaluating the canonical partition function of statistical thermodynamics. Calculations of this type have been performed for many species, and the results are available in convenient tabulations¹⁵. Computer programs¹⁶ are also readily available to perform additional calculations as new or revised spectroscopic data become available. The reference value of the chemical potential for condensed phases is sometimes chosen to be the chemical potential of the pure species at the same temperature and pressure; however, other choices can be made and these are discussed by Kirkwood and Oppenheim⁵. To generate the usual equilibrium constant relations from the chemical potential we need only apply (I. 39) and (I. 40) to the chemical reactions (I. 19) by substituting into the equilibrium relations (I. 22). We will simplify the notation by assuming that we are only interested in the gaseous phase and then suppress the index α . This gives

$$\frac{(n_j/n)}{\prod_{k=1}^l (n_k/n)^{\nu_{kj}}} = K_j \Delta K_j \quad (j = l + 1, \dots, m) \quad (\text{I. 43})$$

where we've assumed the first l species were chosen as components. Here $K_j(T, P)$ is the usual mole fraction equilibrium constant given by

$$\ln K_j \equiv -\frac{1}{RT} \left[{}^0\mu_j - \sum_{k=1}^l {}^0\mu_k \nu_{kj} \right] \quad (j = l + 1, \dots, m) \quad (\text{I. 44})$$

while $\Delta K_j(T, P, n_i^\alpha)$ has a corresponding definition in terms of the deviation from ideality $\Delta\mu_i$.

$$\ln \Delta K_j \equiv -\frac{1}{RT} \left[\Delta\mu_j - \sum_{k=1}^l \Delta\mu_k \nu_{kj} \right] \quad (j = l + 1, \dots, m) \quad (\text{I. 45})$$

NUMERICAL SOLUTION OF NONLINEAR EQUATIONS

In principle, the problem of chemical equilibrium has now been solved. In practice, a great deal remains undone. For example, we must still obtain, from experiment or theory, the dependence of the chemical potential, μ_i^α , on the temperature, pressure and composition variables. This aspect of the problem will not be considered and we will assume μ_i^α is known in subsequent portions of the paper. Perhaps the problem that causes the greatest practical difficulty is the solution of the nonlinear equations that describe equilibrium. In general, these equations cannot be solved in closed form but must be solved numerically by the application of some iteration scheme. The solution of a system of non-

linear equations is not a problem that is unique to thermodynamics but, on the contrary, it is a problem that occurs in all areas of science and engineering. As a result, the literature of numerical analysis contains a number of techniques that can be employed to effect a solution. We shall describe a few of these methods; however, we shall not go into their derivation nor shall we give any detailed discussion of the numerical aspects of these methods. Our primary concern is to briefly present some of the methods that have been successfully used for equilibrium computations in the past and a few others that potentially might be used for this purpose in the future.

The thermodynamic notation of the preceding section is not well suited to a discussion of methods for solving systems of nonlinear equations. In this section we shall use the more concise notation of matrix algebra. Thus, for example, the set of equations ((I. 7), (I. 9)) will be written as

$$\underline{f} = \underline{f}(\underline{x}) = \underline{0} \quad (\text{II. 1})$$

where \underline{f} and \underline{x} are real, N-dimensional column vectors and \underline{x} represents the N independent variables. In our case \underline{x} would stand for the composition variables and possibly the Lagrangian multipliers, the temperature and pressure. Broadly speaking, the techniques for solving nonlinear equations have been divided into two categories by Householder¹⁷. These categories are (1) the functional iteration methods and (2) the descent methods. The functional iteration reduces the problem of solving a system of nonlinear equations to the problem of solving an infinite sequence of linear equations. The descent methods reduce the problem to solving an infinite sequence of single, generally nonlinear, equations. We first turn our attention to the functional iterations.

FUNCTIONAL ITERATIONS

Let \underline{x}^* represent the solution of (II. 1); that is, $\underline{f}(\underline{x}^*) = \underline{0}$. Then the functional iteration is characterized by a vector function $\underline{g}(\underline{x})$ such that

$$\underline{g}(\underline{x}^*) = \underline{x}^* \quad (\text{II. 2})$$

In terms of this function and some initial estimate, \underline{x}_0 , for \underline{x}^* we can define a sequence of vectors \underline{x}_k by the formula

$$\underline{x}_{k+1} = \underline{g}(\underline{x}_k) \quad (\text{II. 3})$$

If \underline{x}_0 is sufficiently close to \underline{x}^* this sequence will converge to \underline{x}^* ¹⁷. Although convergence is thus guaranteed, it is often difficult to obtain an initial estimate that is sufficiently close. This difficulty is common to all functional iterations.

The various functional iterations differ from one another by the choice of $\underline{g}(\underline{x})$. Perhaps the most widely used iteration of this type is the Newton or Newton-Raphson iteration. In this iteration the function $\underline{g}(\underline{x})$ is given by the formula

$$\underline{g}(\underline{x}) = \underline{x} - \underline{J}^{-1}(\underline{x})\underline{f}(\underline{x}) \quad (\text{II. 4})$$

Here $\underline{J}(\underline{x})$ is the Jacobian matrix, that is, the matrix formed from the partial derivatives of \underline{f}

$$\underline{J} = \frac{\partial \underline{f}}{\partial \underline{x}}$$

The equations (II. 3) and (II. 4) can be combined into

$$\underline{J}(\underline{x}_k)(\underline{x}_{k+1} - \underline{x}_k) = -\underline{f}(\underline{x}_k) \quad (\text{II. 5})$$

from which it is apparent that the iteration is obtained by truncating the Taylor expansion of $\underline{f}(\underline{x})$ after the first derivative. Although the iteration will converge for a sufficiently good estimate, the method has some practical difficulties. Not only must one obtain a sufficiently good estimate, which in itself might present a considerable problem, but also at each stage of the iteration the Jacobian \underline{J} must be nonsingular. Additionally, the repeated evaluation of the Jacobian and its inverse will require a considerable amount of computation time if the number of equations, N , is large. It is possible to somewhat compensate for this last difficulty by employing a modified form of Newton's iteration¹⁷⁻¹⁸. In this form of the iteration the Jacobian is not re-evaluated for each iteration but is fixed at its initial value.

$$\underline{g}(\underline{x}) = \underline{x} - \underline{J}^{-1}(\underline{x}_0)\underline{f}(\underline{x}) \quad (\text{II. 6})$$

As a practical matter this form of the iteration should probably only be used in the later stages of a calculation.

Newton's method presupposes that the functional form of $\underline{f}(\underline{x})$ is known since one must be able to calculate the Jacobian. When the functions $\underline{f}(\underline{x})$ are so complex that it becomes impractical to differentiate them or when expressions for the functions are not known, then Newton's iteration cannot be used. The latter situation can arise in thermodynamics when the chemical potential is only available in tabular form. In such a case, it is possible to use a generalized secant method¹⁹⁻²⁰ which is an example of the so-called multipoint iterative methods whose convergence has been discussed by Tornheim²¹.

The multipoint iterative methods are characterized by the fact that no derivatives are required in the evaluation of $\underline{g}(\underline{x})$. The generalized secant method is, in effect, Newton's method with an approximate Jacobian. If \underline{x}_k is the current estimate for \underline{x}^* then an approximate Jacobian can be evaluated with the aid of N auxiliary points \underline{x}_{ki} ($i = 1, 2, \dots, N$) in the vicinity of \underline{x}_k by the formula

$$\underline{J}(\underline{x}_k) \approx \underline{\Delta f}_k [\underline{\Delta x}_k]^{-1} \quad (\text{II. 7})$$

where the matrices $\underline{\Delta f}_k$ and $\underline{\Delta x}_k$ are the matrices whose columns are formed from the column vectors \underline{f} and \underline{x} .

$$\begin{aligned} \underline{\Delta f}_k &= \left(\underline{f}(\underline{x}_{k1}) - \underline{f}(\underline{x}_k), \underline{f}(\underline{x}_{k2}) - \underline{f}(\underline{x}_k), \dots, \underline{f}(\underline{x}_{kN}) - \underline{f}(\underline{x}_k) \right) \\ \underline{\Delta x}_k &= (\underline{x}_{k1} - \underline{x}_k, \underline{x}_{k2} - \underline{x}_k, \dots, \underline{x}_{kN} - \underline{x}_k) \end{aligned} \quad (\text{II. 8})$$

Thus the generalized secant method is defined by the function

$$\underline{g}(\underline{x}) = \underline{x} - (\underline{\Delta x})(\underline{\Delta f})^{-1} \underline{f}(\underline{x}) \quad (\text{II. 9})$$

where the indices on the matrices $\underline{\Delta x}$ and $\underline{\Delta f}$ have been suppressed. This method has the advantage that no derivatives of $\underline{f}(\underline{x})$ need be calculated; however, this means that when the iteration converges, we have only an approximate $\underline{J}(\underline{x}^*)$. Since the Jacobian is needed to calculate the thermodynamic first derivatives by means of (I.30)-(I.34) this means that only approximate values of these derivatives can be obtained.

The last method of the functional iteration type is the method of successive substitution²². It is based on being able to write $\underline{f}(\underline{x})$ in the form

$$\underline{f}(\underline{x}) = \underline{x} - \underline{g}(\underline{x})$$

Thus the function $\underline{g}(\underline{x})$ is defined to be

$$\underline{g}(\underline{x}) = \underline{x} - \underline{f}(\underline{x}) \quad (\text{II. 10})$$

Thus, in relation to Newton's method, the Jacobian is here taken to be the unit matrix.

DESCENT METHODS

The solution of thermodynamic equilibrium problems can be regarded either as the solution of a system of nonlinear equations or, as pointed out in the comment following (I. 16), as the direct minimization of the Gibbs free energy G . In thermodynamics the nonlinear equations themselves arise from the constrained minimization of G . Thus in thermodynamics there is a very direct connection between minimization and the solution of a system of equations. In fact the solution of any system of nonlinear equations can be regarded as the location of the minimum of some function $\psi(\underline{x})$. If the equations (II. 1) arise from the minimization of ψ then

$$\underline{f}(\underline{x}) \equiv \frac{\partial \psi}{\partial \underline{x}} \quad (\text{II. 11})$$

and the connection is immediately apparent. When the functions $\underline{f}(\underline{x})$ are obtained in some other way, then we can always define a suitable function ψ by

$$\psi(\underline{x}) \equiv \frac{1}{2} \underline{f}^T \underline{M} \underline{f} \quad (\text{II. 12})$$

where \underline{f}^T is the transpose of \underline{f} and \underline{M} is any real, positive definite matrix. Because \underline{M} is positive definite the function $\psi(\underline{x})$, as defined by (II. 12), is always positive and vanishes only when \underline{f} itself vanishes. This, in fact, is

the definition of a positive definite matrix. The simplest choice for \underline{M} would be the unit matrix, in which case $\psi(\underline{x})$ is proportional to the sum of the squares of the components of \underline{f} and is a measure of the error. In the following discussion $\psi(\underline{x})$ will represent the objective function to be minimized and could be either the Gibbs function regarded as a function of the ξ_r or the equivalent of (II. 12).

A review of minimization techniques has been given by Spang²³. We shall confine our attention to only a few of the many possibilities. All of the methods that we consider will generate a sequence, \underline{x}_k , of approximations to the minimum, \underline{x}^* , by the formula

$$\underline{x}_{k+1} = \underline{x}_k + \lambda \underline{u}_k \quad (\text{II. 13})$$

The vector \underline{u}_k is arbitrary except that it must not lie in the surface $\psi(\underline{x}) = \text{constant}$ at the point \underline{x}_k . It specifies a direction of descent while the parameter λ determines the size of the step. The methods under consideration differ in the choice of \underline{u}_k ; however, they all essentially determine λ by the requirement that the one-variable function

$$\psi_1(\lambda) \equiv \psi(\underline{x}_k + \lambda \underline{u}_k) \quad (\text{II. 14})$$

be a minimum. This is equivalent to determining λ by solving the equation

$$\underline{u}_k^T \left. \frac{\partial \psi}{\partial \underline{x}} \right|_{\underline{x}=\underline{x}_k+\lambda \underline{u}_k} = 0 \quad (\text{II. 15})$$

where the gradient $\partial \psi / \partial \underline{x}$ is the column vector whose components are the par-

tial derivatives of ψ with respect to the components of \underline{x} . In principle this gives the optimum choice of λ . In practice, however, it is often advantageous to use an approximate value for λ rather than to devote an excessive amount of time to a search for the optimum value. Thus Householder¹⁷ suggests determining an approximate λ by one step of Newton's method applied to (II. 15) with an initial estimate of $\lambda = 0$. Spang²³ suggests some other possibilities. One should also recognize the possibility that an approximate value of λ might be obtained empirically based on experience with related systems of equations.

There are many possibilities for the choice of a direction vector \underline{u}_k . For example, all of the functional iterations discussed previously could be used to supply a direction. Thus from Newton's method (II. 4) we could take

$$\underline{u} = -\underline{J}^{-1}\underline{f} \quad (\text{II. 16})$$

to obtain the descent version of Newton's method. Taking \underline{u} from the method of successive substitutions (II. 10) gives

$$\underline{u} = -\underline{f} \quad (\text{II. 17})$$

In general a large number of choices of this type can be written in the form

$$\underline{u} = -\underline{B}\underline{f} \quad (\text{II. 18})$$

where \underline{B} is some matrix. This form even encompasses the so-called gradient methods where \underline{u} is related to $\partial\psi/\partial\underline{x}$ for either \underline{f} is already the gradient (II. 11) or else from (II. 12) $\partial\psi/\partial\underline{x} = \underline{J}^T \underline{M}\underline{f}$. In particular the method of steepest descent is given by the choice

$$\underline{u} = \frac{\partial\psi}{\partial\underline{x}} \quad (\text{II. 19})$$

Perhaps the simplest choice of a descent direction is to take \underline{u} along one of the coordinate lines. If one selects the j^{th} coordinate line, it then follows from (II.15) that λ is determined so as to make the j^{th} component of the gradient equal to zero by changing only the j^{th} coordinate. This method of operation is known as a univariate or relaxation method. The choice of coordinate lines can be made in a number of ways. For example, they might be taken in sequence or perhaps they might be chosen so as to reduce the largest component of the gradient to zero.

As the final technique for solving systems of nonlinear equations, we will briefly consider a method that is basically a descent method but incorporates some of the features of the multipoint iterations. It possesses the advantage, like the multipoint iterations, of not requiring the calculation of a Jacobian but unlike these methods it gives the correct Jacobian when the iteration converges. Because of these two properties, it should have a considerable utility in thermodynamic calculations. This type of iteration was first proposed by Davidon²⁴ and was subsequently refined by Fletcher and Powell²⁵. Somewhat related algorithms were later suggested by Barnes²⁶, and Broyden²⁷. A numerical comparison of some of these methods was made by Rosen²⁸. The calculation method uses a direction of descent given by (II.18). For the initial iteration the choice of the matrix \underline{B} is quite arbitrary; however, the matrix for subsequent iterations is obtained by continually modifying the initial choice so that at convergence the matrix becomes the Jacobian.

PERTURBATION CALCULATIONS

The foregoing discussion of techniques for solving systems of equations has, of necessity, been somewhat brief. However we must caution the reader

that although, in theory, convergence can be demonstrated for these algorithms, in practice they can encounter convergence difficulties even for relatively simple problems. A few interesting examples of simple but "difficult" problems are given by Turner²⁹. Difficult problems can be solved with a sufficiently good estimate. The problem one must then consider is how to find a good estimate. Perhaps if one knew the solution to a related problem this solution might be used as an initial estimate. This is basically the notion behind perturbation theory. Because of the wide class of thermodynamic equilibrium problems that can now be solved routinely, the potential for the application of perturbation theory clearly exists. To describe this procedure we assume that we have a solvable problem that can be continuously deformed into the actual problem and that in this deformation process the solution of the solvable problem goes continuously into the solution of the actual problem. Thus we consider a system of parameter dependent equations

$$\underline{f}(\underline{x}; \epsilon) = 0 \quad (\text{II. 20})$$

The particular method of parameterization will be left unspecified; however, we will assume that the continuous parameter ϵ is so chosen that

$$\underline{f}(\underline{x}; 0) \equiv \underline{f}^0(\underline{x}) \quad (\text{II. 21})$$

corresponds to the solvable problem and

$$\underline{f}(\underline{x}; 1) \equiv \underline{f}(\underline{x}) \quad (\text{II. 22})$$

corresponds to the actual problem. Since the solution \underline{x}^* is assumed to be a continuous function of ϵ , we can write

$$\underline{x}^* = \underline{x}^*(\epsilon) \quad (\text{II. 23})$$

A Taylor expansion of (II. 23) gives

$$\underline{x}^*(\epsilon + \Delta\epsilon) = \underline{x}^*(\epsilon) + \frac{d\underline{x}^*}{d\epsilon} \Delta\epsilon + \frac{1}{2} \frac{d^2 \underline{x}^*}{d\epsilon^2} (\Delta\epsilon)^2 + \dots \quad (\text{II. 24})$$

If $\underline{x}^*(\epsilon)$ is known and the derivatives appearing on the right-hand side of (II. 24) can be evaluated, then (II. 24) can be used to provide an initial estimate for the solution of $\underline{f}(\underline{x}; \epsilon + \Delta\epsilon)$. This initial estimate can then be refined by any one of the iterations described previously. The required derivatives can be evaluated. For example, by differentiation of (II. 20) with respect to ϵ we obtain

$$\left. \frac{\partial \underline{f}}{\partial \underline{x}} \right|_{\underline{x}^*(\epsilon)} \frac{d\underline{x}^*}{d\epsilon} + \frac{\partial \underline{f}}{\partial \epsilon} = 0 \quad (\text{II. 25})$$

Solving this linear equation we obtain

$$\frac{d\underline{x}^*}{d\epsilon} = -J^{-1}(\underline{x}^*(\epsilon); \epsilon) \frac{\partial \underline{f}}{\partial \epsilon}(\underline{x}^*(\epsilon); \epsilon) \quad (\text{II. 26})$$

Higher derivatives can be obtained by further differentiation of (II. 25) with respect to ϵ . The actual number of terms that must be used in (II. 24) depends on the nature of the equations being solved and on the size of the increment $\Delta\epsilon$. For a sufficiently small increment, it should be possible to use only $\underline{x}^*(\epsilon)$. A technique similar to the discussion given above was described by Freudenstein and Roth³⁰.

LITERATURE SURVEY

All the information that is necessary for an understanding of equilibrium computations has been summarized in the preceeding portions of this paper. We could now carry out a perfunctory literature survey merely by pointing out that a given author calculated equilibrium compositions by combining a particular set of thermodynamic equations with a certain numerical technique. However, this procedure admits only a relatively small number of different combinations, a number considerably smaller than the number of papers cited in the reference list of this review. The inescapable conclusion is that many of these papers must be merely minor variations on a major theme. This is true, but it is equally true that it is just this fine structure that converts a theoretical method into a practical and workable one. There is no pat answer to the question of what constitutes a practical and workable method. Obviously, the method should be reliable and capable of giving the correct answers when properly implemented. It seems to us that it is the implementation that ultimately decides whether or not a method is to be considered acceptable. A technique that is excellent for manual computations might be completely unsuited to machine calculation. Similarly, a very general method designed for application to a wide class of equilibrium problems can be expected to be inferior to a method tailored for a specific problem when both are applied to the same problem. As an extreme example of this we could cite the application of an iterative method to the simple problem of the dissociation of an ideal diatomic gas for which a closed form solution exists. Whenever discussing specific methods we shall try to point out their advantages and disadvantages in an attempt to delineate their appropriate area of application.

We shall try to avoid a discussion of computer programs while looking at the various methods of calculation. But because of the availability and wide spread use of computers, we should mention some points that are pertinent to the philosophy of writing computer programs for chemical equilibrium computations. The kind of program that one writes is largely influenced by the intended application. Let us suppose that we are faced with the problem of doing extensive calculations on a particular chemical system within relatively narrow ranges of the independent parameters and further that the equilibrium calculations are a significant part of the total computational effort. In such a situation it would be judicious to write an equilibrium computation program that would minimize the computation time. This means that we would write a program tailored to the specific problem in which we would take advantage of all the available information, including initial estimates of composition, and in addition would perform algebraically, rather than numerically, as many of the mathematical operations as is possible. On the other hand, if we had the problem of doing calculations on a wide variety of chemical systems with broad ranges in the independent parameters, it would be advantageous to write a very flexible program with no requirements for initial estimates, built-in safeguards to assure numerical convergence, simplified input, and a large amount of internal bookkeeping ability. This approach possesses the advantage that one need write and debug only one computer program that is then instantly available for a broad range of problems. It also has the disadvantage that the computation time for a given chemical system will be somewhat longer than that required by a well-written specific program for the same system. We ourselves have written a broadly disseminated program of the general vari-

ety ³¹⁻³². The report by Erickson, et. al. ³³ should be consulted as an example of the kind of time reduction that is possible with a very specific program. This completes our acknowledgment of the existence of computers and, at least for the balance of this section, we shall try to ignore them.

EQUILIBRIUM CONSTANT METHODS

The early equilibrium calculations were invariably based on the equilibrium constant formulation of the thermodynamic equation (I. 43) and were generally carried out for gas phase equilibria. Usually the effects of non-ideality were neglected by setting ΔK_j equal to unity. Additionally, because the moles, n_i , appeared in the equilibrium constant not only individually but in the combination $n = \sum n_i$, it became convenient to regard n as another independent variable. This in turn required that the defining equation for n (I. 41) be added to (I. 21) and (I. 43) to form the set of equations determining equilibrium conditions for a given temperature and pressure. Because the calculations were done manually, there was an emphasis on performing an algebraic reduction of variables before attempting a numerical solution. The chemical reactions and the associated equilibrium relations were not written in the systematic manner (I. 19) and (I. 43) but were written in a manner that reflected the authors choice of the important equilibria. We will cite only a few of the many examples of this method of operation. Traustel ³⁴, for example, reduced the equations for the gaseous CHON (carbon, hydrogen, oxygen and nitrogen) system to two equations in two unknowns and then solved these by a Newton-Raphson iteration (II. 4). Similarly, Huff and Calvert ³⁵ reduced the equations for the same system to two working equations but then used a graphical method of solution. Donegan and Farber ³⁶, working with

the HO system, solved their two working equations by a special purpose iteration. The iteration was based on an empirical relationship between the estimate for one of the variables and the residual in one of the equations. Martinez and Elverum³⁷ considered the six element system CHONF plus one other halogen. They succeeded in reducing the equations for this system to two quadratics. These quadratics were solved simultaneously by essentially the method of successive substitutions (II. 10) in terms of an assumed value for a parameter that appeared in both equations. Like Huff and Calvert, a graphical technique was used by Sachsel, Mantis and Bell³⁸ to evaluate equilibria in the HOBA1 system.

The use of equilibrium constants has persisted through the years; however, with the introduction of the digital computer the preoccupation with actual algebraic reduction waned. Thus, for example, both Goldwasser³⁹⁻⁴⁰ and Villars⁴¹⁻⁴² used equilibrium constants but made no attempt at an algebraic reduction of variables. In both cases the method of solution was the relaxation method with ξ_r , the extent of reaction, chosen as the independent variables. The function ψ of (II. 12) that was being minimized was essentially the sum of the squares of the equilibrium relations (I. 22). Villars solved the equation corresponding to (II. 15) exactly while Goldwasser suggested using a one term Newton-Raphson approximation.

At a relatively early stage in the history of equilibrium computations, it became apparent that the system of equations could be put into a form that was suitable for solution by the method of successive substitutions. One way to obtain such a form is to work in terms of mole fractions. We will illustrate this for ideal, gaseous phase equilibria. The logarithms of the equilibrium

constants (I. 43) are already in an appropriate form

$$\ln(n_j/n) - \sum_{k=1}^l \nu_{kj} \ln(n_k/n) - \ln K_j = 0 \quad (j = l + 1, \dots, m) \quad (\text{III. 1})$$

The conservation equations (I. 21) and the defining equation for n (I. 41) can easily be rewritten as

$$\sum_{j=1}^m \left(\nu_{kj} - \frac{q_k^0}{q_1^0} \nu_{1j} \right) (n_j/n) - 1 = 0 \quad (k = 2, 3, \dots, l) \quad (\text{III. 2})$$

$$\sum_{j=1}^m (n_j/n) - 1 = 0$$

Now it can be observed that (III. 1) expresses all constituents in terms of the components while (III. 2), because it is linear, can easily be solved for the mole fractions of the components in terms of the constituents. This is precisely what is required to apply the method of successive substitutions. Because of the form of (III. 1) the iteration requires initial estimates only for the component mole fractions in contrast to the usual situation which requires estimates for all the variables. This, basically, is the iteration proposed by Krieger and White⁴³.

The fact that the equations for determining chemical equilibrium can be written in the form (III. 1) and (III. 2) has been used by other people, however not with the successive substitutions iteration. Hilsenrath et. al.⁴⁴ regard (III. 1) as providing the means for effectively eliminating the constituent mole fractions although no actual algebraic reduction of variables is performed.

Their iteration formula for the moles of components can be written for the j^{th} iteration as

$$n_k^{(j+1)} = n_k^{(j)} + \epsilon_k \frac{(q_k^o - q_k^{(j)})}{q_k^{(j)}} n_k^{(j)} \quad (k = 1, 2, \dots, l) \quad (\text{III. 3})$$

where ϵ_k are empirically determined numbers between zero and one and where $q_k^{(j)}$ is defined by

$$q_k^{(j)} = \sum_{i=1}^m \nu_{ki} n_i^{(j)} \quad (k = 1, 2, \dots, l) \quad (\text{III. 4})$$

They chose as components the atomic species ($\nu_{kj} = a_{kj}$). This can be regarded as a descent iteration because of its similarity to (II. 13). The direction of descent is given by (II. 18) and \underline{B} is chosen as diagonal matrix whose elements are $\epsilon_k n_k^{(j)} / q_k^{(j)}$. The numbers ϵ_k not only play the role of λ in (II. 13) but also partially determine the descent direction. Since the direction and magnitude of the step are, in part, determined empirically, no function ψ need be specified. Scully⁴⁵ employs a somewhat related iteration in the sense that successive approximations are also generated by a formula akin to (II. 13). It is, however, a relaxation process since only one component is altered at a time rather than altering all of them simultaneously as is done by Hilsenrath. Scully determines the step size empirically.

Algebraic reduction has not disappeared totally from the equilibrium computations scene. Recently Erickson et. al.³³ have revived the method in an attempt to devise rapid, special purpose computer programs. They have demonstrated that, in principle, it is possible to reduce any ideal gas calculation

to the problem of finding the appropriate root of a high order polynomial in one variable. They acknowledge that, in practice, the complete reduction is well-nigh impossible in a large problem. In relatively simple problems with only a few species the reduction can be carried out, and the resulting polynomial can be treated, for example, by the Newton-Raphson method. Apart from the practical difficulties of generating an explicit expression for the polynomial from the chemical equilibrium equations, this method is beset with severe numerical problems. Wilkinson⁴⁶ points out that the roots of polynomials can be extremely sensitive to relatively small errors in the polynomial coefficients and, in fact, the computed roots may bear no relationship to the actual roots. This is compounded by the fact that in order to determine the equilibrium composition one must find the appropriate root among the many false roots that have been introduced while effecting the reduction to polynomial form. Thus in all but the relatively simple equilibrium problems this method has little to recommend it.

Although all of the methods of calculation that we have discussed to this point have assumed that the system was ideal, the effects of non-ideality can be easily incorporated using the perturbation technique. Thus we would define a parameter dependent equilibrium constant

$$\ln \bar{K}_j(\epsilon) \equiv \ln K_j - \epsilon \ln \Delta K_j \quad (j = l + 1, \dots, m) \quad (\text{III. 5})$$

where ϵ is the perturbation parameter of equations (II. 20) to (II. 26).

The schemes that we have just discussed are, in principle, applicable to any problem. In practice they are best suited to specific problems where one can take advantage of the idiosyncrasies of a specific system. The first for-

mulation in a notation that was suitable for a general problem was given by Brinkley⁴⁷⁻⁴⁹. His procedure was to apply the Newton-Raphson iteration to (I. 21), (I. 22), (I. 41) with the assumption that the thermodynamic state was specified by assigning the temperature and pressure (I. 23). Shortly afterward Huff and co-workers⁵⁰ extended it so that the thermodynamic state could be specified in terms of any two thermodynamic variables and also suggested some minor changes which had important significance for the application of the method. The combination of these two techniques was widely applied by many people^{13, 32, 51-65}. The similarity of the Brinkley and Huff iterations permits us to discuss both of them simultaneously. To do this we will have to deviate slightly from their original presentations, but our changes will not alter the significant aspects of the method.

Our presentation of the Brinkley-Huff method will assume that the thermodynamic state is being specified by assigning the pressure and enthalpy. That is, we will be using equations (I. 21), (I. 22) and (I. 24). In addition, as we've already pointed out, the quantities n^α appear directly in the ideal chemical potential. For this reason it is convenient, but not necessary, to regard the n^α as additional variables that are related to the n_i^α by (I. 41) rather than to regard (I. 41) as the defining equation for the n^α . This ad hoc introduction of p additional variables requires us to augment the equations (I. 21), (I. 22) and (I. 24) with the p extra equations (I. 41). The ideal chemical potential, $\bar{\mu}_i^\alpha$, will now be regarded as an explicit function of n_j^α , n^α , T and P

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\alpha(n_j^\alpha, n^\alpha, T, P) \quad (\text{III. 6})$$

The excess chemical potential, $\Delta\mu_i^\alpha$, will continue to be considered as de-

pending explicitly only on n_j^α , T and P .

$$\Delta \mu_i^\alpha = \Delta \mu_i^\alpha(n_j^\alpha, T, P) \quad (\text{III. 7})$$

The reason for this dichotomous treatment of the chemical potential is that it permits algebraic simplifications in later stages of the development. Finally, for simplicity of notation we shall select the first l species of the gaseous phase ($\alpha = 1$) as the components.

If we take $\ln n_i^\alpha$, $\ln n^\alpha$ and $\ln T$ as the expansion variables then the Newton-Raphson equations (II. 5) have the explicit form

$$\begin{aligned} & \sum_{\beta, k} \left[\delta^{\alpha\beta} (\delta_{jk} + \Gamma_{jk}^{\beta\beta}) - \delta^{\beta 1} \sum_{i=1}^l \nu_{ij} (\delta_{ik} + \Gamma_{ik}^{11}) \right] \Delta \ln n_k^\beta - \left(\Delta \ln n^\alpha - \Delta \ln n^1 \sum_{i=1}^l \nu_{ij} \right) \\ & - \left[\left(H_j^\alpha - \sum_{i=1}^l \nu_{ij} H_i^1 \right) / RT \right] \Delta \ln T = - \left(\mu_j^\alpha - \sum_{i=1}^l \nu_{ij} \mu_i^1 \right) / RT \quad (\alpha = 1, 2, \dots, p; \\ & \quad \quad \quad j = 1, 2, \dots, m) \\ & \sum_{\alpha, j} \nu_{kj} n_j^\alpha \Delta \ln n_j^\alpha = q_k^0 - q_k \quad (k = 1, 2, \dots, l) \\ & \sum_j n_j^\alpha \Delta \ln n_j^\alpha - n^\alpha \Delta \ln n^\alpha = n^\alpha - \sum_i n_i^\alpha \quad (\alpha = 1, 2, \dots, p) \\ & \sum_{\alpha, j} (n_j^\alpha H_j^\alpha / RT) \Delta \ln n_j^\alpha + \left(\sum_{\alpha, j} C_j^\alpha n_j^\alpha / R \right) \Delta \ln T = (H_0 - H) / RT \end{aligned} \quad (\text{III. 8})$$

where all quantities in these equations are evaluated in terms of the current estimates for n_j^α , n^α , and T . The unsymmetric matrix $\underline{\Gamma}$ that appears in these equations is defined as

$$\Gamma_{jk}^{\alpha\beta} \equiv \frac{\partial (\Delta \mu_j^\alpha / RT)}{\partial \ln n_k^\beta} = n_k^\beta \Delta \mu_{jk}^{\alpha\beta} = \delta^{\alpha\beta} \Gamma_{jk}^{\beta\beta} \quad (\text{III. 9})$$

Because $\Delta \mu_j^\alpha$ is homogeneous of degree zero in n_i^α , the matrix $\underline{\Gamma}$ satisfies the two relationships

$$\begin{aligned} \sum_{\beta, k} \Gamma_{jk}^{\alpha\beta} &= 0 = \sum_k \Gamma_{jk}^{\alpha\alpha} \\ \sum_{\alpha, j} n_j^\alpha \Gamma_{jk}^{\alpha\beta} &= 0 = \sum_j n_j^\beta \Gamma_{jk}^{\beta\beta} \end{aligned} \quad (\text{III. 10})$$

The assumption that $\Delta \mu_j^\alpha$ was to be considered only as an explicit function of the n_i^α and not of n^α was made in order to retain these useful properties. The Newton-Raphson equations (III. 8) represent $(p(m + 1) + 1)$ linear equations in a corresponding number of unknowns (note that the first equation contains l identities ($\alpha = 1, j = 1, 2, \dots, l$)). In any problem of practical interest the actual number of equations could easily approach or surpass one hundred. For this reason pragmatic considerations demand that some reduction be made in the number of working equations. Brinkley essentially assumed that Γ could be neglected in (III. 8). We will shortly demonstrate that a reduction in the number of working equations can be achieved without this assumption; however to display the working equations in their usual form, let us neglect Γ . The neglect of Γ in the first member of (III. 8) enables us to solve these equations for the corrections to the moles of constituents in terms of the components. Substitution into the remaining members of (III. 8) produces the reduced number of working equations in the form

$$\begin{aligned}
& \sum_{i=1}^l r_{ki} \Delta \ln n_i^1 + \sum_{\alpha=1}^p \left(\sum_j \nu_{kj} n_j^\alpha \right) \Delta \ln n^\alpha + \left[\left(\sum_{\alpha,j} \nu_{kj} n_j^\alpha H_j^\alpha - \sum_{i=1}^l r_{ki} H_i^1 \right) / RT \right] \Delta \ln T \\
& - \Delta \ln n^1 \sum_{i=1}^l r_{ki} = q_k^0 - q_k + \left(\sum_{\alpha,j} \nu_{kj} n_j^\alpha \mu_j^\alpha - \sum_{i=1}^l r_{ki} \mu_i^1 \right) / RT \quad (k = 1, 2, \dots, l) \\
& \sum_{i=1}^l \left(\sum_j \nu_{ij} n_j^\alpha \right) \Delta \ln n_i^1 + \left[\left(\sum_j H_j^\alpha n_j^\alpha - \sum_{i=1}^l \left(\sum_k \nu_{ik} n_k^\alpha \right) H_i^1 \right) / RT \right] \Delta \ln T \\
& - \Delta \ln n^1 \sum_{i=1}^p \sum_j \nu_{ij} n_j^\alpha = n^\alpha - \sum_i n_i^\alpha + \left(G^\alpha - \sum_{i=1}^l \left(\sum_j \nu_{ij} n_j^\alpha \right) \mu_i^1 \right) / RT \\
& \quad (\alpha = 1, 2, \dots, p) \\
& \sum_{i=1}^l \left[\left(\sum_{\alpha,j} \nu_{ij} H_j^\alpha n_j^\alpha \right) / RT \right] \Delta \ln n_i^1 + \sum_{\alpha} \left(\sum_j n_j^\alpha H_j^\alpha / RT \right) \Delta \ln n^\alpha \\
& + \left[\sum_{\alpha,j} C_j^\alpha n_j^\alpha / R + \sum_{\alpha,j} H_j^\alpha H_j^\alpha n_j^\alpha - \sum_{i=1}^l \sum_{\alpha,j} \nu_{ij} H_j^\alpha n_j^\alpha H_i^1 / R^2 T^2 \right] \Delta \ln T \\
& - \Delta \ln n^1 \sum_{i=1}^l \sum_{\alpha,j} \nu_{ij} H_j^\alpha n_j^\alpha / RT = (H_0 - H) / RT \\
& + \left[\sum_{\alpha,j} n_j^\alpha H_j^\alpha \mu_j^\alpha - \sum_{i=1}^l \left(\sum_{\alpha,j} \nu_{ij} H_j^\alpha n_j^\alpha \right) \mu_i^1 \right] / R^2 T^2
\end{aligned} \tag{III. 11}$$

where

$$r_{ik} = \sum_{\alpha,j} \nu_{ij} \nu_{kj} n_j^\alpha \quad (i, k = 1, 2, \dots, l) \tag{III. 12}$$

These equations can be solved for the component corrections, $\Delta \ln n_i^1$, and the constituent corrections can then be calculated from the first member of (III. 8), again neglecting Γ .

Equations (III. 11) encompass both the Brinkley and the Huff variations of the Newton-Raphson calculation. To obtain the iteration suggested by Brinkley we need only make three specializations: (1) ignore the last equation in (III. 11) and set $\Delta \ln T$ to zero in the other equations; (2) treat the $\Delta \ln n_i^1$ ($i = 1, 2, \dots, l$) and $\Delta \ln n^\alpha$ ($\alpha = 1, 2, \dots, p$) as independent variables and calculate the constituent mole numbers from the components and estimates of the equilibrium constants based on the current compositions; and (3) interpret the logarithmic corrections $\Delta \ln x^{(k)}$ as $(x^{(k+1)} - x^{(k)})/x^{(k)}$. To obtain the Huff variant we must: (1) retain the temperature as a variable; (2) select atomic species as components ($\nu_{ij} = a_{ij}$, $q_k^0 = b_k^0$); (3) treat both components and constituents as independent variables during the iteration; and (4) use all corrections in the logarithmic form rather than the linear form. Items (3) and (4) of the Huff version are quite important from a practical standpoint. For example, the use of logarithmic corrections automatically insures the fact that all variables will remain positive if initially chosen to be positive and thus will satisfy the non-negativity constraints in the mole numbers n_i^α . The disadvantage of treating only the component moles as independent variables is that one needs rather good estimates for the components to obtain a convergent iteration. This problem has prompted some authors to devise schemes for obtaining initial estimates for the Newton-Raphson iteration^{64, 66-67}. An alternate approach to this problem is to select as components only those species that are present in major amounts. This is not completely satisfactory since it creates the problem of changing components during the course of the iteration. This "optimum component" procedure has been used^{52, 62, 68}; however, the problem can be handled in a less complicated manner by treating all species as independent during the

iteration. This often produces a convergent iteration even with relatively poor estimates. This latter method, while less susceptible to divergence, has been known to diverge. The divergent cases can be handled by using a descent Newton iteration.

The basic disadvantage of the working equations (III.11) or of their predecessors (III.8) is the asymmetric treatment of the species. From these equations it is obvious that the components are singled out for preferential treatment. In the case of (III.11) this is more obvious than true since we demonstrated ⁶⁹ that the equations could be put in a symmetric form by a simple transformation that eliminates those linear combination terms in (III.11) that are component dependent. Introducing a variable u_i by the definition

$$\Delta \ln n_i^1 = u_i + (H_i^1/RT) \Delta \ln T - \mu_i^1 + \Delta \ln n^1 \quad (i = 1, 2, \dots, l) \quad (\text{III.13})$$

and substituting this into (III.11) gives as the symmetric equations determining u_i , $\Delta \ln n^\alpha$ and $\Delta \ln T$

$$\begin{aligned} \sum_{i=1}^l r_{ki} u_i + \sum_{\alpha=1}^p \left(\sum_j \nu_{kj} n_j^\alpha \right) \Delta \ln n^\alpha + \left(\sum_{\alpha,j} \nu_{kj} n_j^\alpha H_j^\alpha / RT \right) \Delta \ln T \\ = q_k^0 - q_k + \sum_{\alpha,j} \nu_{kj} n_j^\alpha \mu_j^\alpha / RT \quad (k = 1, 2, \dots, l) \\ \sum_{i=1}^l \left(\sum_j \nu_{ij} n_j^\alpha \right) u_i + (H^\alpha/RT) \Delta \ln T = n^\alpha - \sum_i n_i^\alpha + G^\alpha \quad (\alpha = 1, 2, \dots, p) \\ \sum_{i=1}^l \left[\left(\sum_{\alpha,j} \nu_{ij} H_j^\alpha n_j^\alpha \right) / RT \right] u_i + \sum_{\alpha=1}^p (H^\alpha/RT) \Delta \ln n^\alpha + \left[\sum_{\alpha,j} C_j^\alpha n_j^\alpha / R \right. \\ \left. + \sum_{\alpha,j} H_j^\alpha H_j^\alpha n_j^\alpha / R^2 T^2 \right] \Delta \ln T = (H_0 - H)/RT + \sum_{\alpha,j} H_j^\alpha n_j^\alpha \mu_j^\alpha / R^2 T^2 \end{aligned} \quad (\text{III.14})$$

The substitution of (III. 13) into the first member of (III. 8), neglecting $\underline{\Gamma}$, gives the corrections to all species in the form

$$\Delta \ln n_j^\alpha = - \mu_j^\alpha / RT + \sum_{i=1}^l u_i \nu_{ij} + (H_j^\alpha / RT) \Delta \ln T + \Delta \ln n^\alpha \begin{pmatrix} j = 1, 2, \dots, m \\ \alpha = 1, 2, \dots, p \end{pmatrix} \quad (\text{III. 15})$$

This form (III. 14), (III. 15) of the Brinkley-Huff iteration is computational superior to the original formulation because all species are given an equivalent treatment.

FREE ENERGY MINIMIZATION METHODS

Prior to 1958 all equilibrium computations were carried out using the equilibrium constant formulation of the governing equations. In 1958 White, Johnson and Dantzig⁷⁰ suggested that equilibrium compositions be calculated by "free energy minimization". Their procedure soon captured the fancy of some of the people making thermodynamic calculations, and it became the basis for a number of computer programs⁷¹⁻⁷⁵. The world of equilibrium computations was then divided into two camps, the free energy minimizers, and the reactionary equilibrium constant formulators. It was not long before extravagant claims and counterclaims of guaranteed convergence were heard from proponents of each method. So heated became the controversy that when a panel discussion was arranged to discuss equilibrium computations in 1959⁷⁶, it was necessary to divide the panel into a free energy panel and an equilibrium constant panel. To see what it was that provoked such a controversy let us examine the method of free energy minimization.

As we did in the discussion of Brinkley-Huff iteration we will deviate somewhat from the original presentation. This will enable us to incorporate some

subsequent developments and it will also put the method in proper perspective. We will formulate the method for the case where the thermodynamic state is specified by pressure and enthalpy since this will facilitate a comparison with our development of the Brinkley-Huff method; however, it should be clear that any two thermodynamic variables will suffice. To obtain the method, we need only apply the descent Newton-Raphson method to the equations (I. 7), (I. 24) and the dimensionless form of (I. 9) obtained by dividing the equation by RT . The function ψ to be minimized may be the Gibbs free energy G to which has been added one half the sum of the squares of (I. 7) and (I. 41). It is no restriction to require that the estimates for the Lagrangian multipliers $\pi_i \equiv -\lambda_i/RT$ be taken as zero for each iteration since the multipliers occur linearly in (I. 9). Again, as before, we will use the n^α as independent variables and thus we will add (I. 41) to our set of equations and in addition we will use, except for the π_i , the logarithmic form of the variables in the expansion. With these conditions we obtain as the Newton-Raphson equations

$$\begin{aligned}
 & \sum_{\beta, k} \delta^{\alpha\beta} (\delta_{jk} + \Gamma_{jk}^{\beta\beta}) \Delta \ln n_k^\beta - \sum_{i=1}^l a_{ij} \pi_i - \Delta \ln n^\alpha \\
 & - (H_j^\alpha / RT) \Delta \ln T = - \mu_j^\alpha / RT \quad \left(\begin{array}{l} \alpha = 1, 2, \dots, p \\ j = 1, 2, \dots, m \end{array} \right) \quad (\text{III. 16}) \\
 & \sum_{\alpha, j} a_{kj} n_j^\alpha \Delta \ln n_j^\alpha = b_k^0 - b_k \quad (k = 1, 2, \dots, l) \\
 & \sum_{\alpha, j} n_j^\alpha \Delta \ln n_j^\alpha - n^\alpha \Delta \ln n^\alpha = n^\alpha - \sum_i n_i^\alpha \\
 & \sum_{\alpha, j} (n_j^\alpha H_j^\alpha / RT) \Delta \ln n_j^\alpha + \left(\sum_{\alpha, j} n_j^\alpha C_j^\alpha / R \right) \Delta \ln T = (H_0 - H) / RT
 \end{aligned}$$

The basic similarity of these equations and the corresponding equations (III.8) of the Brinkley-Huff method is now clear; the only difference occurs between the first member of each set. As a matter of fact, if (III.8) is written with atomic species as components and if we eliminate the π_i from (III.16) by using the first l equations of the first member of (III.16) ($\alpha = 1, j = 1, 2, \dots, l$) we then obtain exactly (III.8) because $a_{ij} = \delta_{ij}$ ($j = 1, 2, \dots, l$). But this should have been obvious from the outset since it is quite immaterial whether the Lagrangian multipliers are eliminated prior to linearization or subsequent to linearization. It should also be abundantly clear that neither method can have any inherent advantage; however, this is not meant to imply that "free energy minimization" has no computational advantage. The benefits that exist are associated with the fact that no species are singled out for special handling. This, for example, makes it possible to incorporate the effect of the matrix $\underline{\Gamma}$ into the iteration while still retaining a small set of working equations analogous to (III.14). The corresponding development in the case of (III.8) is considerably more awkward. Although it is desirable to use $\underline{\Gamma}$ in the iteration, it is not absolutely necessary to do so in order to obtain a convergent iteration. However, once the equilibrium compositions have been calculated and one wishes to calculate the thermodynamic derivatives, it then becomes necessary to use $\underline{\Gamma}$ to obtain the correct values for these derivatives.

The equations that must be solved in order to obtain the thermodynamic derivatives C_p , $\partial V/\partial T$ and $\partial V/\partial P$ from (I.30)-(I.32) are very similar to the iteration equations (III.16). This similarity

enables us to give a simultaneous discussion of the procedure for taking account of non-ideal effects. The equations for the derivatives with respect to T are given by the expressions

$$\sum_{\beta, k} \delta^{\alpha\beta} (\delta_{jk} + \Gamma_{jk}^{\beta\beta}) \frac{\partial \ln n_k^\beta}{\partial \ln T} - \sum_{i=1}^l a_{ij} \frac{\partial \pi_i}{\partial \ln T} - \frac{\partial \ln n^\alpha}{\partial \ln T} = H_j^\alpha / RT$$

$$\left(\begin{array}{l} \alpha = 1, 2, \dots, p \\ j = 1 \dots m \end{array} \right)$$

$$\sum_{\alpha, j} a_{kj} n_j^\alpha \frac{\partial \ln n_j^\alpha}{\partial \ln T} = 0 \quad (k = 1, 2, \dots, l) \quad (\text{III. 17})$$

$$\sum_j n_j^\alpha \frac{\partial \ln n_j^\alpha}{\partial \ln T} - n^\alpha \frac{\partial \ln n^\alpha}{\partial \ln T} = 0 \quad (\alpha = 1, 2, \dots, p)$$

The equations that determine the derivatives with respect to P are

$$\sum_{\beta, k} \delta^{\alpha\beta} (\delta_{jk} + \Gamma_{jk}^{\beta\beta}) \frac{\partial \ln n_k^\beta}{\partial \ln P} - \sum_{i=1}^l a_{ij} \frac{\partial \pi_i}{\partial \ln P} - \frac{\partial \ln n^\alpha}{\partial \ln P} = -PV_j^\alpha / RT$$

$$\left(\begin{array}{l} \alpha = 1, 2, \dots, p \\ j = 1, 2, \dots, m \end{array} \right)$$

$$\sum_{\alpha, j} a_{kj} n_j^\alpha \frac{\partial \ln n_j^\alpha}{\partial \ln P} = 0 \quad (k = 1, 2, \dots, l) \quad (\text{III. 18})$$

$$\sum_j n_j^\alpha \frac{\partial \ln n_j^\alpha}{\partial \ln P} - n^\alpha \frac{\partial \ln n^\alpha}{\partial \ln P} = 0 \quad (\alpha = 1, 2, \dots, p)$$

Apart from the fact that the coefficient matrix of (III. 16) has one more row and column than either (III. 17) or (III. 18), the three sets of equations are identical. To illustrate the reduction to a smaller set of working equations

we shall use the more concise matrix notation $\underline{M}\underline{v} = \underline{w}$ to symbolize any one of the three sets of equations (III. 16), (III. 17), or (III. 18). Further, we shall assume that the matrix \underline{M} and the column vectors \underline{v} and \underline{w} have been partitioned so that the set of equations can be written in the form

$$\begin{pmatrix} \underline{M}_{11} & \underline{M}_{12} \\ \underline{M}_{21} & \underline{M}_{22} \end{pmatrix} \begin{pmatrix} \underline{v}_1 \\ \underline{v}_2 \end{pmatrix} = \begin{pmatrix} \underline{w}_1 \\ \underline{w}_2 \end{pmatrix} \quad (\text{III. 19})$$

The column vector \underline{v}_1 is associated with the variables n_j^α while \underline{v}_2 is associated with the remaining variables. If the square submatrix $\underline{M}_{11} = \underline{I} + \underline{\Gamma}$ is assumed to be nonsingular then we can write

$$\underline{v}_1 = \underline{M}_{11}^{-1}(\underline{w}_1 - \underline{M}_{12}\underline{v}_2) \quad (\text{III. 20})$$

This expression can now be used to eliminate \underline{v}_1 from the second member of (III. 19) to give

$$\underline{N}\underline{v}_2 = \underline{y} \quad (\text{III. 21})$$

where

$$\begin{aligned} \underline{N} &\equiv \underline{M}_{22} - \underline{M}_{21}\underline{M}_{11}^{-1}\underline{M}_{12} \\ \underline{y} &\equiv \underline{w}_2 - \underline{M}_{21}\underline{M}_{11}^{-1}\underline{w}_1 \end{aligned} \quad (\text{III. 22})$$

The matrix \underline{N} and the vector \underline{y} both contain the inverse of \underline{M}_{11} which must either be calculated numerically or else must be known as a closed form analytical expression. Numerical inversion of \underline{M}_{11} would defeat our avowed purpose of providing a smaller set of working equations analogous to (III. 14) and a

closed form expression of \underline{M}_{11}^{-1} is not possible under all circumstances.

However, when the contribution of $\underline{\Gamma}$ to \underline{M}_{11} can be regarded as a perturbation, then \underline{M}_{11}^{-1} may be replaced by its iterative expansion

$$\underline{M}_{11}^{-1} = \sum_{k=0}^{\infty} (-1)^k \underline{\Gamma}^k \quad (\text{III. 23})$$

where

$$\underline{\Gamma}^0 \equiv \underline{I}$$

The substitution of (III. 23) into (III. 22) gives as an alternate expression for \underline{N} and \underline{y} .

$$\underline{N} = \sum_{k=0}^{\infty} \underline{N}^{(k)} \quad \underline{y} = \sum_{k=0}^{\infty} \underline{y}^{(k)} \quad (\text{III. 24})$$

where the matrices $\underline{N}^{(k)}$ and the column vectors $\underline{y}^{(k)}$ are defined by

$$\begin{aligned} \underline{N}^{(k)} &= \underline{M}_{22} \delta^{(0,k)} - (-1)^k \underline{M}_{21} \underline{\Gamma}^k \underline{M}_{12} \\ \underline{y}^{(k)} &= \underline{w}_2 \delta^{(0,k)} - (-1)^k \underline{M}_{21} \underline{\Gamma}^k \underline{w}_1 \end{aligned} \quad (\text{III. 25})$$

The index k effectively gives the order to which the perturbation matrix $\underline{\Gamma}$ appears in the various terms. Therefore, we are now in a position to apply conventional perturbation theory to the solution of the reduced set of equations (III. 21). Writing

$$\underline{v}_2 = \sum_{k=0}^{\infty} \underline{v}_2^{(k)} \quad (\text{III. 26})$$

and equating terms in (III. 21) with the same order of perturbation we obtain the usual hierarchy of equations

$$\begin{aligned} \underline{N}^{(0)} \underline{v}_2^{(0)} &= \underline{y}^{(0)} \\ \underline{N}^{(0)} \underline{v}_2^{(k)} &= \underline{y}^{(k)} - \sum_{j=1}^k \underline{N}^{(j)} \underline{v}_2^{(k-j)} \quad (k = 1, 2, \dots) \end{aligned} \quad (\text{III. 27})$$

These expressions can be used to calculate \underline{v}_2 to the desired order of perturbation. The expression for \underline{v}_1 can then be obtained from \underline{v}_2 by using (III. 20).

$$\underline{v}_1 = \sum_{n=0}^{\infty} \underline{v}_1^{(n)} = \sum_{n=0}^{\infty} \left[(-1)^n \underline{\Gamma}^n \underline{w}_1 - \sum_{k=0}^n (-1)^k \underline{\Gamma}^k \underline{M}_{12} \underline{v}_2^{(n-k)} \right] \quad (\text{III. 28})$$

Explicit expressions for the matrices $\underline{N}^{(k)}$ and the vectors $\underline{y}^{(k)}$ can be readily constructed for the iteration equations (III. 16). These can be written in a compact form by first introducing the notation

$$\underline{\Delta\mu}^{\alpha} = \left[\Delta\mu_{jk}^{\alpha\alpha} \right] \quad \underline{n}^{\alpha} = \left[n_j^{\alpha} \delta_{jk} \right] \quad (\text{III. 29})$$

and then defining the sequence of symmetric matrices

$$\begin{aligned} {}^{(0)}\underline{\Lambda}^{\alpha} &= \underline{n}^{\alpha} \\ {}^{(1)}\underline{\Lambda}^{\alpha} &= \underline{n}^{\alpha} \underline{\Delta\mu}^{\alpha} \underline{n}^{\alpha} \\ {}^{(2)}\underline{\Lambda}^{\alpha} &= \underline{n}^{\alpha} \underline{\Delta\mu}^{\alpha} \underline{n}^{\alpha} \underline{\Delta\mu}^{\alpha} \underline{n}^{\alpha} \\ &\dots = \dots \end{aligned} \quad (\text{III. 30})$$

With this notation we have for $\underline{N}^{(n)}$

$$N^{(n)} = (-1)^n \begin{bmatrix} \sum_{\alpha, j, q}^{(n)} \Lambda_{jq}^{\alpha} a_{ij} a_{kq} & \delta^{(n, 0)} \sum_j a_{ij} n_j^{\beta} & \sum_{\alpha, j, q}^{(n)} \Lambda_{jq}^{\alpha} a_{ij} H_q^{\alpha} / RT \\ \delta^{(n, 0)} \sum_q a_{kq} n_q^{\gamma} & 0 & \delta^{(n, 0)} (H^{\gamma} / RT) \\ \sum_{\alpha, j, q}^{(n)} \Lambda_{jq}^{\alpha} H_j^{\alpha} a_{kq} / RT & \delta^{(n, 0)} (H^{\beta} / RT) & \delta^{(n, 0)} \sum_{\alpha, j} n_j^{\alpha} C_j^{\alpha} / R \\ & & + \sum_{\alpha, j, q}^{(n)} \Lambda_{jq}^{\alpha} H_j^{\alpha} H_q^{\alpha} / R^2 T^2 \end{bmatrix} \quad (\text{III. 31})$$

$\left(\begin{array}{l} i, k = 1, 2, \dots, l \\ \gamma, \beta = 1, 2, \dots, p \end{array} \right)$

while the column vector $\underline{y}^{(n)}$ has the form

$$\underline{y}^{(n)} = (-1)^n \begin{bmatrix} \delta^{(n, 0)} (b_i^0 - b_i) + \sum_{\alpha, j, q}^{(n)} \Lambda_{jq}^{\alpha} a_{ij} \mu_q^{\alpha} / RT \\ \delta^{(n, 0)} \left[n^{\gamma} - \sum_j n_j^{\gamma} + G^{\gamma} / RT \right] \\ \delta^{(n, 0)} (H_0 - H) / RT + \sum_{\alpha, j, q}^{(n)} \Lambda_{jq}^{\alpha} H_j^{\alpha} \mu_q^{\alpha} / R^2 T^2 \end{bmatrix} \quad (\text{III. 32})$$

$\left(\begin{array}{l} i = 1, 2, \dots, l \\ \gamma = 1, 2, \dots, p \end{array} \right)$

The expressions for $\underline{N}^{(n)}$ and $\underline{y}^{(n)}$ were considerably simplified by using the

properties (III. 10). The zero order approximation of (III. 27) and (III. 28) is now easily seen to be identical to the modified Brinkley-Huff equations (III. 14) and (III. 15) when the components of the Brinkley-Huff method are atomic species. Equivalently, the identity could be established by writing the free energy equations in terms of components.

The original presentation of the free energy method differed considerably from our discussion. White et al.⁷⁰ derived their equations only for the ideal gas phase and minimized the quadratic approximation to the Gibbs free energy for an assigned temperature and pressure subject to the mass balance constraint (I. 7). Their equations may be obtained from our zero order approximation by taking $p = 1$, deleting the last row and column of $\underline{N}^{(0)}$ and striking out the last element of $\underline{y}^{(0)}$, setting b_i equal to b_i^0 , and interpreting all corrections linearly rather than logarithmically. The implementation of their version of the free energy method requires that the estimates always satisfy the mass balance constraints. In principle this is no problem; however, it does cause unnecessary difficulties in practice. These arise because round-off errors can cause compositions to violate mass balance even though the initial estimates satisfied mass balance. Both Levine⁷⁷ and we⁶⁹ indicated how to modify their equations within the framework of their derivation. The extension of the White method to multiphases and non-ideal systems was done by a number of people⁷⁸⁻⁸¹, all using the quadratic approximation to the Gibbs free energy. We developed the perturbation approach to incorporating the effects of non-ideality on both the iteration and the calculation of thermodynamic derivatives¹⁴. For the sake of completeness, we will now give the formulae for calculating the derivatives C_p/R ,

$\partial \ln V / \partial \ln T$ and $\partial \ln V / \partial \ln P$. In all cases the matrices $\underline{N}^{(n)}$ are the same as (III. 31) with the last row and column deleted. The vectors $\underline{y}^{(n)}$, however, differ from (III. 32). For the temperature derivatives $\underline{y}^{(n)}$ has the form

$$\underline{y}^{(n)} = (-1)^n \begin{bmatrix} - \sum_{\alpha, j, q} {}^{(n)}\Lambda_{jq}^{\alpha} a_{ij} H_q^{\alpha} / RT \\ -\delta^{(n, 0)} (H^{\gamma} / RT) \end{bmatrix} \quad \begin{matrix} (i = 1, 2, \dots, l) \\ (\gamma = 1, 2, \dots, p) \end{matrix} \quad \text{(III. 33)}$$

while for the pressure derivatives it becomes

$$\underline{y}^{(n)} = (-1)^n \frac{P}{RT} \begin{bmatrix} \sum_{\alpha, j, q} {}^{(n)}\Lambda_{jq}^{\alpha} a_{ij} V_q^{\alpha} \\ \delta^{(n, 0)} V^{\gamma} \end{bmatrix} \quad \begin{matrix} (i = 1, 2, \dots, l) \\ (\gamma = 1, 2, \dots, p) \end{matrix} \quad \text{(III. 34)}$$

In terms of the solutions to the hierarchy of equations (III. 27) and (III. 28) the expressions, (I. 30), (I. 31) and (I. 32), for the thermodynamic derivatives become

$$C_P/R = \sum_{r=0}^{\infty} \left[\delta^{(r, 0)} \left(\sum_{\alpha, j} n_j^{\alpha} C_j^{\alpha}/R + \sum_{\alpha} (H^{\alpha}/RT) \left(\frac{\partial \ln n^{\alpha}}{\partial \ln T} \right)^{(0)} \right) \right. \\ \left. + (-1)^r \sum_{\alpha, j, q} {}^{(r)}\Lambda_{jq}^{\alpha} \frac{H_j^{\alpha} H_q^{\alpha}}{R^2 T^2} + \sum_{n=0}^r (-1)^n \sum_{i=1}^l \left(\frac{\partial \pi_i}{\partial \ln T} \right)^{(r-n)} \sum_{\alpha, j, q} {}^{(n)}\Lambda_{jq}^{\alpha} a_{kq} H_j^{\alpha} / RT \right] \quad \text{(III. 35a)}$$

$$\begin{aligned} \frac{\partial \ln V}{\partial \ln T} = \frac{1}{V} \sum_{r=0}^{\infty} \left[\delta(r, 0) \left(\sum_{\alpha, j} n_j^{\alpha} \frac{\partial V_j^{\alpha}}{\partial \ln T} + \sum_{\alpha} V^{\alpha} \left(\frac{\partial \ln n^{\alpha}}{\partial \ln T} \right)^{(0)} \right) \right. \\ \left. + (-1)^r \sum_{\alpha, j, q} (r)_{\Lambda_{jq}}^{\alpha} \frac{V_j^{\alpha} H_q^{\alpha}}{RT} + \sum_{n=0}^r (-1)^n \sum_{i=1}^l \left(\frac{\partial \pi_i}{\partial \ln T} \right)^{(r-n)} \sum_{\alpha, j, q} (n)_{\Lambda_{jq}}^{\alpha} a_{iq} V_j^{\alpha} \right] \end{aligned} \quad (\text{III. 35b})$$

$$\begin{aligned} \frac{\partial \ln V}{\partial \ln P} = \frac{1}{V} \sum_{r=0}^{\infty} \left[\delta(r, 0) \left(\sum_{\alpha, j} n_j^{\alpha} \frac{\partial V_j^{\alpha}}{\partial \ln P} + \sum_{\alpha} V^{\alpha} \left(\frac{\partial \ln n^{\alpha}}{\partial \ln P} \right)^{(0)} \right) \right. \\ \left. - (-1)^r \frac{P}{RT} \sum_{\alpha, j, q} (r)_{\Lambda_{jq}}^{\alpha} V_j^{\alpha} V_q^{\alpha} + \sum_{n=0}^r (-1)^n \sum_{i=1}^l \left(\frac{\partial \pi_i}{\partial \ln P} \right)^{(r-n)} \sum_{\alpha, j, q} (n)_{\Lambda_{jq}}^{\alpha} a_{iq} V_j^{\alpha} \right] \end{aligned} \quad (\text{III. 35c})$$

In addition to these derivatives with respect to T and P we could also calculate derivatives with respect to the independent parameters b_i^0 . These would be significant in the application of thermodynamics to fluid dynamical problems when one assumes that the flow field is characterized by local thermodynamic equilibrium. The resulting formulae are similar to (III. 35) and therefore we will not reproduce them here.

The free energy method that we have just discussed was shown to be a descent Newton method with the objective function chosen to be essentially the Gibbs free energy. This choice of the objective function could easily be supplanted by any other suitable test function, and thus it seems inappropriate to label the method by a particular choice of test function. There is another method, due to Naphtali⁸²⁻⁸³ that perhaps seems more worthy of the name. He regards the Gibbs free energy as a function of the extent of reaction variables ξ_r and then uses the method of steepest descent to minimize G for assigned values of

temperature and pressure. The components of the gradient vector are just the equilibrium constant expressions as is apparent from (I.15)

$$\frac{\partial G}{\partial \xi_r} = \sum_{\alpha, j} \mu_j^\alpha A_{j r}^\alpha$$

Because the ξ_r are essentially used as the independent variables, the estimates for the composition variables must satisfy the mass balance constraints. This causes the same problems here as in White's original version of the descent Newton calculation. This calculation suffers from the same drawbacks that any equilibrium constant method must endure; that is, one must write appropriate chemical reactions and one must make a judicious choice of components. Snow⁸⁴ has suggested two changes to improve the method. The first of these is to use a weighting matrix \underline{B} (II.18) that is diagonal with the r^{th} diagonal element being chosen as the smallest mole number in the r^{th} reaction. Second, he suggests that "parallel reactions" be written which, in effect, means making a more appropriate choice of components.

Dobbins⁸⁵ has used what could be considered a univariate version of Naphtali's iteration. The direction of descent is along the coordinate line ξ_r that has the largest component of the gradient. In addition he uses atomic species as components and uses an approximate form for the Gibbs free energy during the calculations in order to reduce the calculating time.

Story and Van Zeggeren⁸⁶ used a slightly different approach in the calculation of equilibrium compositions of an ideal gaseous phase at an assigned temperature and pressure. Instead of working with the moles n_i (the phase index has been suppressed because only the gas phase is considered) they essentially introduce logarithmic variables by defining variables z_i by the

relationships

$$n_i = n_i^0 e^{z_i}$$

The n_i^0 plays the role of the current estimate of composition. They obtain a set of equations analogous to (I. 7) and (I. 9) by minimizing the Gibbs free energy subject to the constraints that \underline{z} is a unit vector and that mass-balance is preserved. These equations are then solved for \underline{z} by one step of a Newton-Raphson iteration with $\underline{z} = 0$ as an initial estimate. To facilitate the computations of \underline{z} some terms in the Newton-Raphson equations are neglected. The length of the step in the direction \underline{z} is then obtained so as to minimize the Gibbs free energy.

We've gone into considerable detail in the exposition of methods for calculating equilibria in the presence of chemical reactions. Concomitantly we've slighted the calculation of phase equilibria and ignored the problems associated with obtaining solutions to (I. 26) and (I. 27). However, when thermodynamic data are available, the same kinds of calculational methods can be applied to the computation of phase equilibria as are used in the calculation of reaction equilibria. The only real difference is that in phase equilibria each species is a component whereas in reaction equilibria some species are components and others are constituents.

This concludes our review of calculation methods; however, we still wish to express our opinion on what is the best method of calculation. We feel that any method of calculation that can be made reliable is a good method when equilibrium compositions are the only concern. If, however, thermodynamic derivatives must also be calculated then the scale shifts strongly to the descent

Newton method. In particular we mean the iteration equations in the form (III. 16) or the reduced form (III. 27) and (III. 28). The reason for this is that the iteration and the calculation of derivatives are cast in the same form. With the other iteration methods, it is necessary to write one program to calculate compositions and another to calculate the derivatives since these can only be calculated from (III. 17) and (III. 18) or their counterparts in the Brinkley-Huff calculation. The Brinkley-Huff equations for calculating derivatives are identical to (III. 17) and (III. 18) in the ideal case; however, when non-ideality must be taken into account, then (III. 17) and (III. 18) are preferred because they lead, in a relatively simple manner, to reduced working equations. It might be argued that thermodynamic derivatives are relatively unimportant and that when they are required they can easily be approximated by the non-reacting contributions to (I. 30), (I. 31), and (I. 32). Thus it would seem to indicate that the choice of a method based on its ability to calculate derivatives has no significance. Such an argument is fallacious on both counts. First, thermodynamic derivatives are significant for many applications of thermodynamics. Second, we will show shortly, by numerical example, that in many cases the contributions of the reactive part far exceed the non-reactive contributions to the thermodynamic derivatives.

EXISTENCE OF SOLUTIONS

Our discussion of the numerical methods that can be used to generate solutions of the thermodynamic equations has completely ignored the possibility that these solutions might not be unique. That is, such solutions could be either global minima or else they might merely be local minima of the Gibbs free energy. Thermodynamically the local minima correspond to the so-called

metastable states while global minima correspond to true equilibrium states. Such a question, while important, cannot be given a general answer because the answer depends upon the shape of the Gibbs free energy surface for the system under consideration. The Gibbs free energy varies from system to system because it reflects the varying degree of non-ideality present in each system. A definitive answer can only be given for ideal systems for which an analytical expression for the Gibbs function is known. Hancock and Motzkin⁸⁷ investigated a system composed of an ideal gaseous phase and pure condensed phases while Shapiro and Shapley⁸⁸ examined a system in which all phases were ideal. The conclusion in these studies of ideal systems is that if a solution exists it will be unique.

APPLICATIONS

The previous sections have reviewed the thermodynamic relationships and numerical techniques which permit the calculation of equilibrium compositions, thermodynamic properties, and thermodynamic first derivatives for mixtures. Theoretically calculated properties have been used in a wide variety of practical applications in chemistry and chemical engineering such as the analysis and design of chemical processing equipment, heat exchangers, steam power plants, engines, turbines, compressors, nozzles, and shock tubes.

The usefulness of theoretical thermodynamic properties in predicting actual results depends largely on how closely the assumptions used in the calculations approximate physical reality. In some cases significantly different values may be obtained from various assumptions. In this section a few examples have been selected (a) to illustrate the calculation and use of thermodynamic properties and (b) to point out differences due to several assumptions. These examples

include (1) calculation of flame temperatures, (2) calculation of specific heat and other derivatives, (3) isentropic expansion, (4) use of derivatives to predict effect of change of an initial condition on some final condition of a thermodynamic process, and (5) use and effect of a convergence control factor λ .

Numerical data, which we will use to illustrate the examples, are given in Tables I to IV. These tables are direct computer output and contain some notation to the left of the numerical data which is intended to be similar to that used in this paper, but whose similarity is not always immediately obvious. This lack of similarity is due to the fact that the printer does not contain Greek letters, lower case letters, and subscripts. Thus, for example, P_0/P appears in the tables as PO/P and C_P as CP. Chemical formulas in the tables also differ somewhat from their usual representation. Each chemical element in the chemical formula of a species is followed by a numerical value even when it is unity (as in equation (I.6)), and the phase is indicated between parentheses. For example, gaseous H_2O is given as H2O1(G). We will clarify other notation in these tables during subsequent discussion.

All the examples selected are for one phase, ideal gas systems. Before proceeding with the examples it would be well to clarify what we mean by an ideal gas. The chemical potential of an ideal gas $\bar{\mu}_i^1$ is given by equation (I.40). For this gas the partial molar volume is

$$V_i^1 = RT/P \quad (IV.1)$$

Equation (IV.1) together with equation (I.29) gives the familiar equation of state

$$PV = \sum_i n_i RT = nRT \quad (IV.2)$$

Equation (IV. 2) applies to an ideal gas in the sense that no interparticle forces are assumed to exist. There is no restriction, however, as to whether the n_i remain constant or are variable as a result of a change in system temperature and/or pressure. Thermodynamic texts usually assume ideal gases to be only those for which the n_i in equation (IV. 2) remain constant or, equivalently, those for which the internal energy U satisfies

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad (\text{IV. 3})$$

The only criterion necessary for a gaseous mixture to be considered ideal is equation (IV. 2). A gas which, in addition to equation (IV. 2), also obeys equation (IV. 3) is a special case of an ideal gas. We will refer to ideal gaseous mixtures which obey both equations (IV. 2) and (IV. 3) (n_i constant) as nonreacting; while those mixtures to which equation (IV. 2) applies but equation (IV. 3) does not (n_i variable), we will refer to as reacting.

CALCULATION OF FLAME TEMPERATURE

Theoretical flame temperatures are useful for many engineering applications. They indicate the maximum temperature at which thermal energy released during chemical reactions will be available for conversion to other energy forms such as kinetic energy or work, and they also indicate possible problems relating to materials and cooling.

Equilibrium compositions and adiabatic flame temperatures for specified reactants may be obtained from the solutions of iteration equations (III. 14) or the first member of (III. 27). (The second member of (III. 27) is identically zero for the case of ideal gases.) However, the results so obtained depend consid-

erably on which species are assumed to exist in the reacted mixture. For example, for a stoichiometric mixture of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ at a temperature of 298.15°K , the combustion temperature is calculated to be 4998°K if H_2O is assumed to be the only combustion product. If, however, other species such as H , H_2 , HO_2 , O , O_2 and OH are also assumed to exist and the combustion pressure is assumed to be 50 atmospheres, the combustion temperature is calculated to be 3636°K . The results for this particular calculation are shown in the first column of Table I corresponding to the pressure ratio $P_0/P = 1$. Other parts of this table and Table II will be discussed in the later examples.

The conclusion to be reached from this example is that one should include as possible constituents all species which are considered likely to be significant for some set of conditions. Unfortunately, for complex systems it is difficult, if not impossible, to predict a priori which species are significant for all possible conditions. For example, in the C, H, O, N, F, Cl system, we might initially consider the 69 gaseous species indicated in Table III. Depending on the various atom ratios which might be selected and the temperature and pressure defining the thermodynamic state, some of these species will sometimes be significant and other times insignificant.

This is the type of situation for which the general computer programs discussed in section III are particularly well suited, in that a priori decisions do not have to be made as to which species to include or exclude. For example, consider the reaction of perchloryl fluoride (ClO_3F) with unsymmetrical dimethyl hydrazine ($\text{C}_2\text{H}_8\text{N}_2$). The results for the stoichiometric reaction of $\text{C}_2\text{H}_8\text{N}_2 + 2\text{ClO}_3\text{F}$ are given in Table III for a pressure of 1 atmosphere and for several temperatures from 500° to 5000°K . Of the 69 species considered,

22 have a mole fraction greater than 0.000005 for at least some of the specified conditions. At the two lowest temperatures selected (500° and 1000° K), only the five most stable species have a mole fraction greater than 0.000005.

CALCULATION OF SPECIFIC HEAT AND OTHER DERIVATIVES

Thermodynamic derivatives have many applications in chemical processes. For example, specific heat, which is one of the most commonly used thermodynamic derivatives, appears in applications such as heat transfer calculations, isentropic or isenthalpic relationships, or shock wave parameter calculations. As will be made apparent by the discussion and numerical examples that follow, the assumption of reacting or nonreacting mixtures may affect considerably the computed values of thermodynamic derivatives. In addition, as we will show in later sections, relationships involving these derivatives which are often valid for nonreacting mixtures may not be valid for reacting mixtures.

A knowledge of specific heat and two other first derivatives such as $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ permit one to obtain relationships among all thermodynamic first derivatives by use of tables such as devised by Bridgman⁴. We will first give some discussion relating to the evaluation of these three derivatives and then give some numerical examples to illustrate differences in values between reacting and nonreacting mixtures.

Expressions for evaluating C_P , $\partial V/\partial T$ and $\partial V/\partial P$ are given in equations (I. 30) to (I. 32). Values of $\partial n_i^{\alpha}/\partial P$ which are needed in these equations may be obtained by solution of equations (III. 17) and (III. 18). Alternatively, expressions for C_P and the volume derivatives in logarithmic form, $\partial \ln V/\partial \ln T$ and $\partial \ln V/\partial \ln P$, are also given in equations (III. 35). Since we are dealing only with ideal gases in our examples, we will suppress the index α and we

will need just the zeroth order derivatives in equation (III. 35); i. e., $\partial \pi_i^{(0)} / \partial \ln T$, $(\partial \ln n / \partial \ln T)^{(0)}$, $\partial \pi_i^{(0)} / \partial \ln P$, and $(\partial \ln n / \partial \ln P)^{(0)}$. These zeroth order derivatives may be obtained from the solution of the first member of equation (III. 27) where $\underline{N}^{(0)}$ is given by (III. 31) and $\underline{y}^{(0)}$ by (III. 33) and (III. 34).

Prior to solving equations (III. 17) and (III. 18) (or the first member of equation (III. 27)) an explicit equation of state is needed in order to obtain the V_i^α . For the case of gases only ($\alpha = 1$), Michels¹³ has evaluated the V_i^1 for a non-ideal equation of state. For gases behaving ideally, equation (IV. 2) applies.

For the case of a nonreacting gas obeying equation of state (IV. 2) and equation (IV. 3), equations (I. 30) to (I. 32) become

$$C_P = \sum_{i=1}^m C_i n_i$$

$$(\partial \ln V / \partial \ln T)_P = 1 \quad (IV. 4)$$

$$(\partial \ln V / \partial \ln P)_T = -1$$

The logarithmic form of the volume derivatives was selected to indicate percentage changes between reacting and nonreacting mixtures in the numerical examples which follow.

The data in Tables I, III, and IV illustrate the differences in magnitude between derivatives for reacting and nonreacting mixtures. The data show that for the same temperature, pressure, and equilibrium compositions two sets of values exist for these derivatives. The first set of values is for reacting mixtures and is obtained from the contribution of both terms in equations

(I. 30) to (I. 32), whereas the second set is for nonreacting mixtures and includes the first term only (eq. (IV. 4)). The differences in these two sets may be large or small depending on the contribution of the second term. Thus in Table III, at $T = 500^\circ \text{K}$, the two sets of derivatives are equal, but at $T = 3500^\circ \text{K}$ the values for C_p are 2.91166 and 0.38301 cal/gm $^\circ\text{K}$ for reacting and nonreacting mixtures respectively.

Table IV is given to further illustrate that these differences may be dramatically large. The data in Table IV are for a stoichiometric $\text{H}_2\text{-O}_2$ mixture at a pressure of 0.001 atmospheres and at several temperatures from 1600° to 3200°K . The largest differences occurred at $T = 2600^\circ \text{K}$, where values for C_p are 23.61233 and 0.76922 cal/gm $^\circ\text{K}$ for reacting and nonreacting mixtures respectively. Thus, in this instance, the contribution of the second term in equation (I. 30) due to composition changes produced by a change in temperature is many times greater than the contribution due to the heat capacities of the equilibrium species at the given temperature. Similar large differences due to the assumption of reacting or nonreacting mixtures are also found in calculated values of heat conductivity. Svehla⁸⁹ gives an extensive tabulation of thermodynamic and transport properties for the $\text{H}_2\text{-O}_2$ system. Large differences, although not as dramatic as the one just illustrated for specific heat, are also found in the volume derivatives in Table IV.

The existence of two sets of derivatives may lead one to ask which set is "correct". Unfortunately, thermodynamics cannot settle the question inasmuch as the correct answer is determined by the kinetics of the reactions involved. The two sets of values represent the extreme limits of infinitely fast

reactions and infinitely slow reactions. If a process is such that the important reactions involved have time to reach equilibrium or near-equilibrium, then the reacting values are probably more nearly correct; contrarily, for slow reactions, the values of the nonreacting mixture are probably preferable. For intermediate situations, neither assumption may be satisfactory and calculations using rate constants should be made⁹⁰.

ISENTROPIC PROCESSES

Isentropic processes represent a good approximation to many actual processes. They are used in thermodynamic cycle analyses involving expansions or compressions, in various flow processes such as flow through a nozzle, or in the calculation of parameters such as the velocity of sound. In analyses involving isentropic processes, one often would like to predict conditions at the end of a process from a knowledge of conditions at the beginning of the process. For example, knowing the pressure and temperature or pressure and volume at the beginning of a process, one might like to know the temperature or volume corresponding to an assigned pressure at the end of the process.

Relationships between temperature, pressure and volume for an isentropic process involving a nonreacting ideal gas are found in any elementary thermodynamic textbook. These relationships include the following:

$$T/T_o = (P/P_o)^{(\gamma-1)/\gamma} \quad (\text{IV. 5})$$

and

$$PV^\gamma = P_o V_o^\gamma \quad (\text{IV. 6})$$

where

$$\gamma = C_P/C_V \quad (\text{IV. 7})$$

In equations (IV. 5) and (IV. 6), γ is assumed to be constant or an average value between the initial and final states of the process. Another common expression involving γ , which is also based on an isentropic relationship, is for the velocity of sound

$$a = \sqrt{\gamma nRT} \quad (\text{IV. 8})$$

Here n must be taken as the moles per unit mass.

Equations (IV. 5), (IV. 6) and (IV. 8) usually give reasonably accurate results for nonreacting ideal gas mixtures. Unfortunately, because of their ubiquitousness in the literature, these equations are often mistakenly used for reacting ideal gas mixtures for which they do not apply. We will first present relationships that are similar in appearance to those of equations (IV. 5), (IV. 6) and (IV. 8) and which do apply for reacting as well as nonreacting mixtures. We will then illustrate these relationships with some numerical examples.

To obtain these relationships we will need to evaluate the two isentropic derivatives $(\partial \ln T / \partial \ln P)_S$ and $(\partial \ln P / \partial \ln V)_S$ in terms of C_P , $(\partial \ln V / \partial \ln T)_P$, and $(\partial \ln V / \partial \ln P)_T$:

$$\left(\frac{\partial \ln T}{\partial \ln P} \right)_S = \frac{PV}{T} \left(\frac{\partial \ln V}{\partial \ln T} \right)_P / C_P \quad (\text{IV. 9})$$

and

$$\left(\frac{\partial \ln P}{\partial \ln V}\right)_S = \frac{C_P}{C_V \left(\frac{\partial \ln V}{\partial \ln P}\right)_T} \quad (\text{IV. 10})$$

where

$$C_V \equiv \left(\frac{\partial E}{\partial T}\right)_V = C_P + \frac{PV}{T} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P^2 \bigg/ \left(\frac{\partial \ln V}{\partial \ln P}\right)_T \quad (\text{IV. 11})$$

Equation (IV. 10) may be written

$$\gamma_S = - \gamma / (\partial \ln V / \partial \ln P)_T \quad (\text{IV. 12})$$

where

$$\gamma_S \equiv - \left(\frac{\partial \ln P}{\partial \ln V}\right)_S \quad (\text{IV. 13})$$

The calculation of $(\partial \ln P / \partial \ln V)_S$ permits one to evaluate the velocity of sound according to the relationship

$$a^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = - \frac{P}{\rho} \left(\frac{\partial \ln P}{\partial \ln V}\right)_S \quad (\text{IV. 14})$$

where ρ is density.

In the case of a nonreacting gas, the relationships in equations (IV. 9), (IV. 10), and (IV. 11) reduce to

$$\left(\frac{\partial \ln T}{\partial \ln P}\right)_S = \frac{R}{C_P} = \frac{\gamma - 1}{\gamma} \quad (\text{IV. 15})$$

$$-\left(\frac{\partial \ln P}{\partial \ln V}\right)_S \equiv \gamma_S = \gamma \quad (\text{IV. 16})$$

$$C_P - C_V = R \quad (\text{IV. 17})$$

Integration of equations (IV. 9) and (IV. 10), assuming $(\partial \ln T / \partial \ln P)_S$ and $(\partial \ln P / \partial \ln V)_S$ are constant or represent some mean value over the interval of integration, and using the identity of equation (IV. 13) gives

$$T/T_0 = (P/P_0)^{(\partial \ln T / \partial \ln P)_S} \quad (\text{IV. 18})$$

$$PV^{\gamma_S} = P_0 V_0^{\gamma_S} \quad (\text{IV. 19})$$

For practical applications, only the exponent at the initial point may be available for use in equations (IV. 18) and (IV. 19).

We may write equation (IV. 14) as

$$a = \sqrt{\gamma_S n R T} \quad (\text{IV. 20})$$

Here, as in (IV. 8), n must be on a per unit mass basis. From the definitions of equations (IV. 15) and (IV. 16), it may be seen that equations (IV. 5), (IV. 6) and (IV. 8) for nonreacting mixtures are just special cases of equations (IV. 18), (IV. 19) and (IV. 20), respectively.

We will use the data in Tables I and II to illustrate the use (and misuse) of equations (IV. 5) and (IV. 18) and also equations (IV. 8) and (IV. 20). Table I presents the data for stoichiometric H_2-O_2 at several specified pressures and at constant entropy. These data represent an isentropic process where the data in each column are the equilibrium properties at the temperature and

pressure shown. Table II presents similar data to that of Table I with the important difference that species composition is assumed fixed (nonreacting) for all the tabulated columns. The fixed composition is taken to be that corresponding to equilibrium composition in the first column of Table I ($T = 3636^{\circ}\text{K}$) and is shown again at the bottom of Table II.

It may be noted that for nonreacting mixtures the values in each column for the pair γ and γ_s given in Table I are equal as are also the values for the pair $(\partial \ln T / \partial \ln P)_S$ and $(\gamma - 1)/\gamma$. (In Tables I to IV, γ is labeled as GAMMA, γ_s as GAMMA(S) and $(\partial \ln T / \partial \ln P)_S$ as (DLT/DLP)S). This is to be expected according to equations (IV.15) and (IV.16). In contrast to this, the corresponding pairs of derivatives for reacting mixtures (defined by equations (IV.9) to (IV.13)) vary considerably as may be observed in Table I.

Let us now consider the problem of estimating the temperature which would result from an isentropic expansion over a pressure ratio P_0/P of 50, assuming that we are starting from the first point in Tables I and II. For the nonreacting mixture, from Table II and using equation (IV.5), we obtain

$$T = 3636(1/50)^{0.16636} = 1896^{\circ}\text{K}$$

Considering the long extrapolation from 3636°K , the estimate of 1896°K compares reasonably well with the accurately calculated value of 1826°K given in Table II.

For the case of a reacting mixture, we will start from the same point as in the previous example but will now use the data of Table I. If equation (IV.5), which we have just illustrated for a nonreacting gas, were mistakenly used to estimate T for a reacting gas (using the equilibrium value of $(\gamma - 1)/\gamma = 0.15908$), the result would be

$$T = 3636(1/50)^{0.15908} = 1952^{\circ} \text{ K}$$

This estimate of 1952° K compares very poorly with the accurately calculated value of 2613° K given in Table I. If, on the other hand, the correct formula (IV.18) were used, we obtain

$$T = 3636(1/50)^{0.08830} = 2574^{\circ} \text{ K}$$

This estimate of 2574° K compares well with the accurately calculated value of 2613° K .

We will now look briefly at the values of velocity of sound for stoichiometric $\text{H}_2\text{-O}_2$ in Table IV. Velocity of sound (or Mach number) appears in applications such as the determination of shock wave parameters⁹¹ or detonation velocities⁹². Values for nonreacting mixtures are obtained from equation (IV.8) using γ , and for reacting mixtures from equation (IV.20) using γ_s . For example, at $T = 2600^{\circ} \text{ K}$, $a = 1843.3$ and 1628.6 m/sec for nonreacting and reacting mixtures respectively. If equation (IV.8) were mistakenly used for the reacting gas (using $\gamma = 1.32619$ instead of $\gamma_s = 1.09756$), one would obtain the incorrect value $a = 1790 \text{ m/sec}$.

The previous illustrations indicate the need to understand the circumstances under which approximate relationships such as equations (IV.4) and (IV.8) are useful and also when they should carefully be avoided.

EFFECT OF CHANGE IN INITIAL CONDITIONS ON END POINT OF A PROCESS

We have previously discussed⁹³ some thermodynamic derivatives which deal with the effect of a change in initial conditions on the end point of a process. The following discussion summarizes the pertinent parts of that presentation and gives some additional derivatives.

As discussed in the first section of this paper, all thermodynamic properties of a system of known composition can be specified uniquely in terms of any two thermodynamic functions, say α and β , which can be regarded as the coordinates of a two-dimensional space. At any point (α, β) , not only are all the thermodynamic properties of the system determined, but it is also possible to determine the rate of change of these properties along some curve in (α, β) space. If, for example, ψ is a third thermodynamic function, the derivative $(\partial\beta/\partial\alpha)_{\psi}$ expresses the rate of change of β with respect to α along a curve of constant ψ . This partial derivative is the usual thermodynamic first derivative which appears in thermodynamic textbooks and which we have discussed so far in this paper.

By a process in thermodynamics we mean that a system originally at some point (α_0, β_0) has moved to a new point (α, β) where (α, β) may differ by an infinitesimal or by a finite amount from (α_0, β_0) . An infinitesimal process can be completely characterized by a derivative of the form $(\partial\beta/\partial\alpha)_{\psi}$. A finite process can be specified by giving a starting point (α_0, β_0) , a path (say a curve of constant ψ), and one of the coordinates of the end point α . For a given path, the only independent variables of the process are the coordinates of the initial point (α_0, β_0) and a coordinate, say α , of the final point. The other coordinate of the final point, β , and all other thermodynamic functions are dependent variables in the process.

Let φ be any dependent thermodynamic variable associated with the end point of a finite process. The rates of change of φ with respect to the independent thermodynamic variables of the process are of two different types. For a change in α , the usual type of derivative $(\partial\varphi/\partial\alpha)_{\psi}$ is needed. However, for

a change in one of the coordinates of the initial points, derivatives of the type $(\partial\varphi/\partial\alpha_0)_{\beta_0}$ and $(\partial\varphi/\partial\beta_0)_{\alpha_0}$ are needed. Expressions for the latter type of derivative will now be obtained.

For a process taking place along a curve of constant ψ

$$\psi_0(\alpha_0, \beta_0) = \psi(\alpha, \beta) = \psi(\alpha, \varphi) \quad (\text{IV. 21})$$

Whatever change in ψ_0 results from a change in the initial point (α_0, β_0) must be equal to the change in ψ . This may be expressed in differential form as

$$\left(\frac{\partial\psi_0}{\partial\alpha_0}\right)_{\beta_0} d\alpha_0 + \left(\frac{\partial\psi_0}{\partial\beta_0}\right)_{\alpha_0} d\beta_0 = \left(\frac{\partial\psi}{\partial\alpha}\right)_{\varphi} d\alpha + \left(\frac{\partial\psi}{\partial\varphi}\right)_{\alpha} d\varphi \quad (\text{IV. 22})$$

Imposing alternately the conditions of constant α_0 and constant β_0 gives the following two desired expressions for the partial derivatives of a function at the end point of a process with respect to the initial coordinates:

$$\left(\frac{\partial\varphi}{\partial\beta_0}\right)_{\alpha_0} = \frac{(\partial\psi_0/\partial\beta_0)_{\alpha_0}}{(\partial\psi/\partial\varphi)_{\alpha}} + \left(\frac{\partial\varphi}{\partial\alpha}\right)_{\psi} \left(\frac{\partial\alpha}{\partial\beta_0}\right)_{\alpha_0} \quad (\text{IV. 23})$$

$$\left(\frac{\partial\varphi}{\partial\alpha_0}\right)_{\beta_0} = \frac{(\partial\psi_0/\partial\alpha_0)_{\beta_0}}{(\partial\psi/\partial\varphi)_{\alpha}} + \left(\frac{\partial\varphi}{\partial\alpha}\right)_{\psi} \left(\frac{\partial\alpha}{\partial\alpha_0}\right)_{\beta_0} \quad (\text{IV. 24})$$

In equations (IV.23) and (IV. 24) all the derivatives in the right-hand side except $(\partial\alpha/\partial\beta_0)_{\alpha_0}$ and $(\partial\alpha/\partial\alpha_0)_{\beta_0}$ are the standard thermodynamic first derivatives and can be immediately evaluated. The two exceptions can be evaluated for a specified

form of a relation which expresses the end point of a process in terms of the initial point

$$\alpha = \alpha(\alpha_0, \beta_0) \quad (\text{IV. 25})$$

Two forms of Equation (IV. 25) are considered in this paper: $\alpha = k_1$ and $\alpha = k_2 \alpha_0$, where k_1 and k_2 are constants. For $\alpha = k_1$, equations (IV. 23) and (IV. 24) reduce to

$$\left(\frac{\partial \varphi}{\partial \beta_0} \right)_{\alpha_0, \alpha} = \left(\frac{\partial \psi_0}{\partial \beta_0} \right)_{\alpha_0} / \left(\frac{\partial \psi}{\partial \varphi} \right)_{\alpha} \quad (\text{IV. 26})$$

$$\left(\frac{\partial \varphi}{\partial \alpha_0} \right)_{\beta_0, \alpha} = \left(\frac{\partial \psi_0}{\partial \alpha_0} \right)_{\beta_0} / \left(\frac{\partial \psi}{\partial \varphi} \right)_{\alpha} \quad (\text{IV. 27})$$

For the particular choice $\alpha = k_2 \alpha_0$, equations (IV. 23) and (IV. 24) give

$$\left(\frac{\partial \varphi}{\partial \beta_0} \right)_{\alpha_0, \alpha_0 / \alpha} = \left(\frac{\partial \psi_0}{\partial \beta_0} \right)_{\alpha_0} / \left(\frac{\partial \psi}{\partial \varphi} \right)_{\alpha} \quad (\text{IV. 28})$$

$$\left(\frac{\partial \varphi}{\partial \alpha_0} \right)_{\beta_0, \alpha_0 / \alpha} = \left(\frac{\partial \psi_0}{\partial \alpha_0} \right)_{\beta_0} / \left(\frac{\partial \psi}{\partial \varphi} \right)_{\alpha} + \frac{\alpha}{\alpha_0} \left(\frac{\partial \varphi}{\partial \alpha} \right)_{\psi} \quad (\text{IV. 29})$$

It may be seen that the right-hand sides of equations (IV. 26) and (IV. 28) are identical.

Two common processes to which equations (IV. 27) to (IV. 29) apply are isentropic and isenthalpic. For an isentropic process we can make the following associations: $\psi_0 = S_0$ and $\psi = S$. In addition, we can use temperature and pressure to specify the thermodynamic state and therefore make the fol-

lowing additional associations: $\beta_o = T_o$, $\alpha_o = P_o$, $\alpha = P$, and $\alpha_o/\alpha = P_o/P$.

Equations (IV. 27) to (IV. 29) then become

$$\left(\frac{\partial \varphi}{\partial P_o}\right)_{T_o, P} = \left(\frac{\partial S_o}{\partial P_o}\right)_{T_o} / \left(\frac{\partial S}{\partial \varphi}\right)_P \quad (\text{IV. 30})$$

$$\left(\frac{\partial \varphi}{\partial T_o}\right)_{P_o, P_o/P} = \left(\frac{\partial S_o}{\partial T_o}\right)_{P_o} / \left(\frac{\partial S}{\partial \varphi}\right)_P \quad (\text{IV. 31})$$

$$\left(\frac{\partial \varphi}{\partial P_o}\right)_{T_o, P_o/P} = \left(\frac{\partial S_o}{\partial P_o}\right)_{T_o} / \left(\frac{\partial S}{\partial \varphi}\right)_P + \frac{P}{P_o} \left(\frac{\partial \varphi}{\partial P}\right)_S \quad (\text{IV. 32})$$

Equations (IV. 30) to (IV. 32) have been evaluated for $\varphi = \ln T$, H , and $\ln V$ differentiated with respect to $\ln P_o$ and $\ln T_o$ and the results are given in Table V.

For an isenthalpic process we can make the same associations as in the previous case except that now $\psi_o = H_o$ and $\psi = H$. For this case, equations (IV. 27) and (IV. 29) become

$$\left(\frac{\partial \varphi}{\partial P_o}\right)_{T_o, P} = \left(\frac{\partial H_o}{\partial P_o}\right)_{T_o} / \left(\frac{\partial H}{\partial \varphi}\right)_P \quad (\text{IV. 33})$$

$$\left(\frac{\partial \varphi}{\partial T_o}\right)_{P_o, P_o/P} = \left(\frac{\partial H_o}{\partial T_o}\right)_{P_o} / \left(\frac{\partial H}{\partial \varphi}\right)_P \quad (\text{IV. 34})$$

$$\left(\frac{\partial \varphi}{\partial P_0}\right)_{T_0, P_0/P} = \left(\frac{\partial H_0}{\partial P_0}\right)_{T_0} \left/ \left(\frac{\partial H}{\partial \varphi}\right)_P \right. + \frac{P}{P_0} \left(\frac{\partial \varphi}{\partial P}\right)_H \quad (\text{IV. 35})$$

Equations (IV. 33) to (IV. 35) have been evaluated for $\varphi = \ln T$, S , and $\ln V$ differentiated with respect to $\ln P_0$ and $\ln T_0$ and are also given in Table V.

Changes in $\ln \varphi$ due to a change in initial conditions can be estimated by using the first term in a Taylor's expansion; that is,

$$\Delta \ln \varphi = \left(\frac{\partial \ln \varphi}{\partial \ln P_0}\right) \Delta \ln P_0 + \left(\frac{\partial \ln \varphi}{\partial \ln T_0}\right) \Delta \ln T_0 \quad (\text{IV. 36})$$

Either correction or both may be used in (IV. 36).

In Table V, numerous expressions appear which involve groups of terms such as PV/T or PV/TC_P . For ideal gases, the equation of state is given by (IV. 2), i.e., $PV/T = nR$. If H is given in cal/gm and C_P and S in cal/gm⁰K as in Tables I to IV, then $R = 1.98726$ cal/mole⁰K. The volume derivatives needed to evaluate the expressions in Table V are given in Tables I to IV using the following notation: $(\partial \ln V / \partial \ln T)_P$ is $(DLV/DLT)_P$ and $(\partial \ln V / \partial \ln P)_T$ is $(DLV/DLP)_T$.

One numerical example will be given to illustrate use of these derivatives. We will use the data in Table I which are for an isentropic process. The problem may be stated as follows: Starting with data for an initial point of $P_0 = 50$ atm and $T_0 = 3636^0$ K and a final point of $P = 1$ atm and $T = 2613^0$ K, calculate the temperature at $P = 1$ atm for an isentropic expansion from

$P_o = 25$ atm and $T_o = 3636^\circ$ K. This involves the derivative

$(\partial \ln T / \partial \ln P_o)_{T_o, P}$. Using the expression in Table V for equation (IV. 30) with $\varphi = \ln T$ and the data from Table I we obtain

$$\begin{aligned} \left(\frac{\partial \ln T}{\partial \ln P_o} \right)_{T_o, P} &= - \frac{P_o V_o}{T_o C_P} \left(\frac{\partial \ln V_o}{\partial \ln T_o} \right)_{P_o} = \frac{-n_o R}{C_P} \left(\frac{\partial \ln V_o}{\partial \ln T_o} \right)_{P_o} \\ &= \frac{-(0.06384)(1.98726)(1.89599)}{1.93619} = -0.12423 \end{aligned}$$

From (IV. 36), with $\ln \varphi = \ln T$ and $\Delta \ln T_o = 0$,

$$\Delta \ln T = \left(\frac{\partial \ln T}{\partial \ln P_o} \right)_{T_o, P} \Delta \ln P_o = -0.12423(-0.69315) = +0.086110$$

$$\ln T = \ln 2613 + 0.086110 = 7.95435$$

$$T = 2848^\circ \text{ K}$$

The estimate of 2848° K compares fairly well with an accurately calculated value of 2820° K.

ITERATION AND CONVERGENCE

A discussion was given in Sections II and III of various computational methods for obtaining chemical equilibrium compositions and the problems of obtaining convergence in iterative calculations. With the exception of the trivial case for which a closed form solution exists, each computational method uses a set of iterative working equations. As a result, in order to insure con-

vergence, each iterative method must be concerned with controlling the step size of corrections and/or with obtaining good initial estimates.

In this section we will give an example to illustrate the iterative process which starts with arbitrary initial estimates. For this purpose we have chosen the method and program with which we are most familiar³¹⁻³² and which were used to obtain all of the numerical results given in the tables. This descent method uses the Newton-Raphson iterative equations (III. 14) with atomic species as components (or, for the case of ideal gases, the first part of equation (III. 27) with $N^{(0)}$ and $y^{(0)}$ given by equations (III. 31) and (III. 32)). This method requires no special initial estimates for composition (an arbitrary estimate is used by the program) and no constraints on mass balance or equilibrium relationships during iteration.

The problem selected is the determination of the equilibrium composition of a stoichiometric mixture of a hydrocarbon $(CH_2)_x$ and elemental oxygen O_2 at a temperature of $300^\circ K$ and a combustion pressure of $P = 0.01 \text{ atm}$. We realize that little chemical intuition is required to permit one to correctly assume that the significant gaseous species resulting from this reaction would be CO_2 and H_2O . However, the point of this example is not to select the best method of solution but rather to show that convergence is possible using arbitrary estimates which may be very poor.

The course of the iteration will be indicated by two parameters: (1) the function ψ (equation (II. 12) with \underline{M} taken as the unit matrix), and (2) the free energy per gram of the mixture. For convenience we will call ψ the error parameter. In addition, we will discuss the step size control parameter λ (equation (II. 13)).

A brief discussion of the control factor λ was given in Section II where we pointed out that an optimum λ could be obtained by minimizing ψ . Further, in Section III we indicated that an optimum λ could also be determined by the Gibbs free energy to which has been added one half the sum of the squares of (I. 7) and (I. 41). However, for observing the course of iteration, G alone is adequate. We use an empirically determined λ such that

$$|\Delta \ln n| \leq 2 \quad (\text{IV. 37})$$

$$\Delta \ln(n_i/n) \leq 2 \text{ for } \ln(n_i/n) \geq -18.5 \quad (\text{IV. 38})$$

$$\Delta \ln(n_i/n) \leq -9.212 - \ln(n_i/n) \text{ for } \ln(n_i/n) < -18.5 \quad (\text{IV. 39})$$

For each iteration, the restrictions given by equations (IV. 37) and (IV. 38) limit the number of moles n and the mole fraction of each currently significant species ($n_i/n > \sim 10^{-8}$) to an increase $\leq e^2$. Equation (IV. 39) limits the mole fraction of each currently insignificant species ($n_i/n < \sim 10^{-8}$) from becoming larger than $\sim 10^{-4}$. Restrictions of the type given by equations (IV. 37) to (IV. 39) are necessary to control the overcorrecting which might otherwise occur when the current estimate is far from the final solution.

The error parameter ψ is composed of three terms which show the combined error in mass balance, number of moles, and chemical potential

$$\psi = \frac{1}{2} \left[\sum_{i=1}^l (b_i^o - b_i)^2 + \left(n - \sum_{j=1}^m n_j \right)^2 + \sum_{j=1}^m \left(\frac{\mu_j^1}{RT} - \sum_{i=1}^l \frac{\mu_i^1}{RT} a_{ij} \right)^2 \right] \quad (\text{IV. 40})$$

The Gibbs free energy per gram of the current mixture at each iteration is given by

$$\frac{G}{\sum_{i=1}^m n_i M_i} = \frac{\sum_{i=1}^m n_i \mu_i}{\sum_{i=1}^m n_i M_i} \quad (\text{IV. 41})$$

where M_i is the molecular weight of the i^{th} species.

For the first iteration, based on 1 gram of mixture, we will arbitrarily assume $n = 1$ and an equal mole fraction for each of 20 gaseous species (C, CH, CH₂, CH₃, CH₄, CO, CO₂, C₂, C₂H₂, C₂H₄, C₂O, C₃, H, HCO, HO₂, H₂, H₂O, O, OH, and O₂). In Table VI we show λ , ψ , and $G/\sum n_i M_i$ for each iteration from 0 to 29. The zeroth iteration corresponds to the initial estimate. The parameters ψ and $G/\sum n_i M_i$ are also given in figure 1.

The control factor λ , which is given in Table VI, is necessary to prevent divergence. It may be seen that λ is less than 1 for the first four iterations and also for the 14th through 18th iterations. If no control factor were used, the corrections to compositions for some species would have been so large that the numerical values would have exceeded the maximum size number permitted by the computer ($\sim 10^{38}$). For those iterations where $\lambda < 1$, the particular species whose corrections determined λ are shown in Table VI. For this example the controlling species were CO₂, CO, CH₄ and H₂O. However, for other problems or for this problem with other initial estimates, any species might control λ .

An initial control on step size ($\lambda < 1$) might have been expected for the first few iterations where composition, mass, and equilibrium relationships

are far from their final values. However, once the full correction has been applied ($\lambda = 1$ from iteration 5 to 13), it might seem surprising to see extremely tight controls on correction step size again being necessary (iterations 14 to 18). The reason this occurs is that with poor initial estimates, it is temporarily possible for one or more significant species to be made extremely small. This occurred in this example for H_2O . To compensate for this small value of H_2O , the correction equations at iteration 14 called for extremely large corrections which, if permitted, would have greatly overcorrected H_2O . The control factor λ reduced these large corrections for several iterations until the full correction could again be permitted.

The progress of the convergence may be followed in Table VI or in figure 1. It may be seen that for all iterations either ψ , $G/\sum n_i M_i$, or usually both decreased. The small increase in ψ at the last iteration simply indicates loss of numerical significance when convergence is essentially reached. In the third iteration $G/\sum n_i M_i$ increased. If a mass constraint were imposed in addition to controlling step sizes, the free energy would have moved continuously toward a minimum. However, in a method such as the one that is being used in this example, mass may vary at each iteration until convergence is reached, and free energy does not necessarily move continuously toward a minimum.

This can be visualized by considering a simple system composed of one chemical element with gm-atoms b_1^0 and two species with moles n_1 and n_2 and having stoichiometric coefficients a_{11} and a_{12} respectively. If mass is constrained during the iterative process, then, at any step in the iteration

$$a_{11}n_1 + a_{12}n_2 = b_1^0 \quad (\text{IV. 42})$$

If mass is permitted to vary, its value b_1 is given by

$$a_{11}n_1 + a_{12}n_2 = b_1 \quad (\text{IV. 43})$$

Figure 2 is a sketch of free energy with contour lines representing lines of constant Gibbs free energy. Also shown in figure 2 are a solid line and a dashed line. The solid line is a plot of equation (IV. 42), with mass constrained at the value b_1^0 . Starting at point A, for the first iteration, the free energy decreases continuously to the solution at B. The dashed line indicates the free energy which could result from an iteration with mass unconstrained. Starting the first iteration at point C, the free energy reaches a temporary minimum at D, increases to E, and then decreases again until finally the dashed line approaches the line AB as the mass converges to b_1^0 .

The previous discussion of free energy is not intended to imply an advantage for constraining mass during iteration. On the contrary, as pointed out in Section III, with mass constrained the calculations introduce mass balance errors that lead continuously to mass imbalance for which there is no effective removal mechanism. Therefore it is a computational advantage not to impose mass constraints. This may be accomplished by including the terms $(b_i^0 - b_i)$ in equation (III. 32).

The convergence example was given to indicate that convergence in chemical equilibrium calculations is usually possible with a descent Newton-Raphson method in spite of rather poor initial estimates. The fact that the 29 iterations were necessary to obtain convergence simply indicates that the

initial estimates were quite poor. Typical problems, that appear more difficult to solve than the example problem, require considerably fewer iterations. For instance, consider the results in Table III which are for a problem involving 69 possible species. For the first point shown ($T = 5000^{\circ} \text{K}$), for which arbitrary estimates of composition were also used, 18 iterations were required. Each of the remaining 9 points started with the solution to the previous point for its initial estimate and required an average of 5.4 iterations for convergence.

SUMMARY

The calculation of complex chemical equilibria is an interplay of thermodynamic fundamentals and numerical analysis. In our review we have tried to consider both aspects of the problem without placing undue emphasis on either. Thus we have contrasted the two alternate, but equivalent, formulations of the conditions of chemical equilibrium: first as a minimization of the Gibbs free energy and second as a set of equilibrium constant relations. Next we considered some of the different numerical techniques that could be used in equilibrium computations and how some of these were implemented by various people. Finally we looked at some applications of the calculated results.

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TABLE I. - THERMODYNAMIC PROPERTIES FOR AN ISENTROPIC PROCESS ASSUMING EQUILIBRIUM COMPOSITION

		Reactants: $H_2 + 0.5 O_2$											
		1.000	10.000	20.000	25.000	30.000	40.000	50.000	100.000	400.000	500.000	1000.000	1000.000
P/P		1.000	5.000	2.500	2.000	1.667	1.250	1.000	0.5000	0.1250	0.1000	0.0500	0.0500
P, ATM		36.6	2990	2823	2771	2728	2663	2613	2459	2150	2099	1935	1935
T, DEG K		381	2958	5503	6716	7907	10230	12492	23219	79592	96876	177475	177475
V, CC/G		0.06384	0.0028	0.05936	0.05908	0.05886	0.05852	0.05827	0.05754	0.05639	0.05625	0.05589	0.05589
N, MOLES/G		0.0	-936.8	-1176.2	-1249.7	-1308.4	-1398.9	-1467.2	-1669.4	-2031.0	-2084.1	-2239.9	-2239.9
M, CAL/G		3.8451	3.8451	3.8451	3.8451	3.8451	3.8451	3.8451	3.8451	3.8451	3.8451	3.8451	3.8451
S, CAL/(G)(K)		15.665	16.590	16.846	16.926	16.990	17.088	17.162	17.379	17.735	17.779	17.892	17.892
M, MOL WT													
DERIVATIVES (REACTING MIXTURE)													
(DLV/DLP)T		-1.05240	-1.03129	-1.02541	-1.02359	-1.02213	-1.01990	-1.01822	-1.01336	-1.00566	-1.00472	-1.00242	-1.00242
(DLV/DLT)P		1.89599	1.65197	1.55118	1.53093	1.50594	1.46617	1.43516	1.33930	1.16449	1.14053	1.07313	1.07313
CP, CAL/G		2.72389	2.38266	2.20834	2.14609	2.09319	2.00627	1.93619	1.70665	1.23047	1.15785	0.95338	0.95338
GAMMA, CP/CP		1.18918	1.15346	1.14544	1.14321	1.14153	1.13918	1.13762	1.13455	1.13999	1.14286	1.15518	1.15518
GAMMA(S), (DLP/DLKH)S		1.12996	1.11840	1.11706	1.11686	1.11682	1.11696	1.11727	1.11960	1.13357	1.13749	1.15339	1.15339
SOUND VEL, A, M/SEC		1476.8	1298.7	1247.5	1232.9	1221.2	1203.0	1189.2	1147.6	1069.0	1055.7	1018.4	1018.4
(DLT/DLP)S		0.08830	0.08305	0.08340	0.08376	0.08415	0.08499	0.08583	0.08973	0.10605	0.11011	0.12563	0.12563
(GAMMA-LI)/GAMMA		0.15908	0.13304	0.12697	0.12527	0.12399	0.12218	0.12097	0.11859	0.12280	0.12501	0.13593	0.13593
DERIVATIVES (NONREACTING MIXTURE)													
(DLV/DLP)T		-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000
(DLV/DLT)P		1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
CP, CAL/G		0.76257	0.74052	0.73294	0.73037	0.72823	0.72474	0.72194	0.71266	0.69040	0.68517	0.57151	0.57151
GAMMA, CP/CP		1.19956	1.19298	1.19182	1.19155	1.19136	1.19114	1.19103	1.19111	1.19375	1.19459	1.19819	1.19819
GAMMA(S), (DLP/DLKH)S		1.19956	1.19298	1.19182	1.19155	1.19136	1.19114	1.19103	1.19111	1.19375	1.19459	1.19819	1.19819
SOUND VEL, A, M/SEC		1521.6	1337.1	1288.5	1273.5	1261.3	1242.3	1227.8	1183.7	1097.0	1082.9	1037.9	1037.9
(DLT/DLP)S		0.16636	0.16177	0.16095	0.16075	0.16062	0.16046	0.16039	0.16045	0.16231	0.16290	0.15541	0.15541
(GAMMA-LI)/GAMMA		0.16636	0.16177	0.16095	0.16075	0.16062	0.16046	0.16039	0.16045	0.16231	0.16290	0.15541	0.15541
MOLE FRACTIONS													
H1(G)		0.04020	0.02036	0.01542	0.01395	0.01280	0.01107	0.00981	0.00636	0.00181	0.00137	0.00048	0.00048
H2(G)		0.00013	0.00002	0.00001	0.00001	0.00001	0.00001	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000
H2(G)		0.12915	0.08921	0.07649	0.07235	0.06897	0.06362	0.05948	0.04673	0.02318	0.01989	0.01110	0.01110
H2O(G)		0.66758	0.79128	0.82672	0.83785	0.84682	0.86072	0.87129	0.90258	0.95548	0.96234	0.97989	0.97989
H1(G)		0.01898	0.00847	0.00612	0.00545	0.00493	0.00417	0.00362	0.00221	0.00053	0.00039	0.00012	0.00012
H1(G)		0.10523	0.06028	0.04828	0.04461	0.04169	0.03723	0.03390	0.02437	0.00963	0.00789	0.00374	0.00374
H2(G)		0.03673	0.03037	0.02596	0.02378	0.02247	0.020318	0.02190	0.01776	0.00937	0.00811	0.00457	0.00457

TABLE II. - THERMODYNAMIC PROPERTIES FOR AN ISENTROPIC PROCESS ASSUMING FIXED* COMPOSITION

Reactants: $H_2 + 0.5 O_2$

P/P	1.000	10.000	20.000	25.000	30.000	40.000	50.000	100.000	400.000	500.000	1000.000
P, ATM	50.00	5.000	2.500	2.000	1.667	1.250	1.000	0.5000	0.1250	0.1000	0.0500
T, DEG K	5036	2451	2164	2078	2009	1904	1826	1597	1204	1148	985
V, CC/G	381	3133	5915	7257	8576	11160	13666	25760	90107	109950	202700
M, MOLLS/G	0.06384	0.06384	0.05384	0.05384	0.06384	0.06384	0.06384	0.06384	0.06384	0.06384	0.05384
M, CAL/G	0.0	-879.6	-1082.3	-1142.3	-1189.6	-1261.0	-1313.8	-1464.1	-1709.2	-1742.5	-1836.1
S, CAL/(G)(K)	3.8451	7.6411	7.6411	7.5411	7.6411	7.6411	7.6411	7.6411	7.6411	7.6411	7.6411
M, MOL WT	15.665	15.665	15.665	15.665	15.665	15.665	15.665	15.665	15.665	15.665	15.665

DERIVATIVES (NONREACTING MIXTURE)

(DLV/DLPT)	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000
(DLV/DLTP)	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
CP, CAL/G	0.76257	0.71553	0.69673	0.69026	0.68482	0.67601	0.66898	0.64625	0.59814	0.59025	0.55503
GAMMA, CP/CV	1.19956	1.21550	1.22261	1.22517	1.22736	1.23101	1.23400	1.24425	1.26918	1.27375	1.28385
SOUND VEL, A, M/SEC	1521.6	1386.9	1353.4	1342.3	1333.2	1319.1	1308.2	1274.3	1203.5	1191.2	1150.5
(GAMMA-1)/GAMMA	0.16636	0.17729	0.18208	0.18379	0.18524	0.18766	0.18963	0.19630	0.21209	0.21492	0.22412

*COMPOSITION FIXED AT THE EQUILIBRIUM COMPOSITION OF THE FIRST POINT

MOLE FRACTIONS

H1(G)	0.04020										
O1(G)	0.01898	H1O2(G)	0.00013	H2(G)	0.12915	H2O1(G)	0.66758				
		O1H1(G)	0.10523	O2(G)	0.03873						

TABLE III. - THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURES AND PRESSURE

[illegible]

TABLE IV. - THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURES AND PRESSURE

Reactants: H ₂ + 0.5 O ₂																
P, ATM	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G	U, G/G
T, DEG K	3800	3600	3400	3200	3000	2800	2600	2400	2200	2000	1800	1600	1400	1200	1000	800
W, CC/G	5188333	49102623	46248747	43177742	39469673	33469673	23848788	15495967	11445288	9509328	8295523	7306905	6306905	5306905	4306905	3306905
N, MOLES/G	U.16639	U.16622	U.15576	U.15443	U.16000	U.14567	U.11178	U.07868	U.06330	U.05794	U.05517	U.05565	U.05517	U.05517	U.05517	U.05517
H, CAL/G	11980.2	11794.9	11578.2	11262.8	10609.0	8819.2	4793.9	803.6	-1148.3	-1944.8	-2295.8	-2439.3	-2439.3	-2439.3	-2439.3	-2439.3
S, CAL/(G)K	9.7841	9.7340	9.6720	9.5761	9.3641	8.7431	7.2470	5.6552	4.8114	4.4344	4.2505	4.1374	4.1374	4.1374	4.1374	4.1374
M, MJL WT	6.610	6.616	6.633	6.682	6.747	6.865	6.946	7.009	7.073	7.137	7.201	7.265	7.329	7.393	7.457	7.521
DERIVATIVES (REACTING MIXTURE)																
(DLV/DLP)T	-1.00000	-1.00182	-1.00451	-1.01242	-1.03756	-1.11226	-1.20831	-1.34661	-1.50573	-1.70197	-1.93431	-2.20093	-2.50093	-2.83482	-3.19482	-3.58093
(DLV/DLP)P	1.01184	1.02832	1.07455	1.21638	1.70649	3.27879	5.62061	4.58921	2.54375	1.51669	1.14736	1.03482	1.03482	1.03482	1.03482	1.03482
CP, CAL/G	U.89076	U.97781	1.23705	2.08583	5.06184	14.23512	23.61233	14.53616	6.02867	2.50421	1.22513	0.78509	0.78509	0.78509	0.78509	0.78509
GAMMA, CP/UV	U.01221	U.55410	1.44113	1.29823	1.21416	1.24464	1.32619	1.24623	1.14674	1.11508	1.13562	1.17746	1.17746	1.17746	1.17746	1.17746
GAMMA(S), (DLP/DLH)S	1.01092	1.55134	1.43466	1.28227	1.17022	1.11901	1.09756	1.08689	1.08518	1.09745	1.13075	1.17643	1.17643	1.17643	1.17643	1.17643
SOUND VEL, A, M/SEC	2910.1	2778.2	2592.9	2368.5	2161.6	1948.1	1628.6	1306.4	1121.8	1028.3	975.0	933.3	933.3	933.3	933.3	933.3
(DLT/DLP)S	U.37559	U.54738	U.26615	U.19087	U.10725	U.06668	U.05288	U.04937	U.05316	U.06974	U.10454	U.14578	U.14578	U.14578	U.14578	U.14578
(GAMMA-1)/GAMMA	U.37975	U.35657	U.30610	U.22970	U.17639	U.19655	U.24596	U.19758	U.12797	U.10401	0.11943	0.15072	0.15072	0.15072	0.15072	0.15072
DERIVATIVES (NONREACTING MIXTURE)																
(DLV/DLP)T	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000
(DLV/DLP)P	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
CP, CAL/G	U.83284	U.83163	U.83027	U.82817	U.82309	U.80727	U.76922	U.72794	U.70056	U.67942	U.65863	U.63863	U.63863	U.63863	U.63863	U.63863
GAMMA, CP/UV	1.05842	1.05889	1.05771	1.05170	1.02997	1.05907	1.40604	1.27356	1.21927	1.20405	1.20405	1.21057	1.21057	1.21057	1.21057	1.21057
GAMMA(S), (DLP/DLH)S	1.05842	1.05889	1.05771	1.05170	1.02997	1.05907	1.40604	1.27356	1.21927	1.20405	1.20405	1.21057	1.21057	1.21057	1.21057	1.21057
SOUND VEL, A, M/SEC	2952.7	2872.9	2787.2	2688.2	2551.2	2299.4	1843.3	1414.1	1189.1	1077.1	1006.1	946.7	946.7	946.7	946.7	946.7
(DLT/DLP)S	U.39702	U.39719	U.39676	U.39456	U.38649	U.35859	U.28878	U.21480	U.17984	U.16948	U.15948	U.17394	U.17394	U.17394	U.17394	U.17394
(GAMMA-1)/GAMMA	U.39702	U.39719	U.39676	U.39456	U.38649	U.35859	U.28878	U.21480	U.17984	U.16948	U.15948	U.17394	U.17394	U.17394	U.17394	U.17394
MOLE FRACTIONS																
H1(G)	U.66615	U.66552	U.66389	U.65922	U.64436	U.59238	U.43546	U.20344	U.05993	U.01182	U.00153	U.00012	U.00012	U.00012	U.00012	U.00012
H2(G)	U.00037	U.00083	U.00204	U.00556	U.01681	U.05292	U.12992	U.16510	U.11429	U.05332	U.01831	U.00457	U.00457	U.00457	U.00457	U.00457
H2O1(G)	U.00000	U.00000	U.00001	U.00010	U.00104	U.01234	U.10713	U.39388	U.70544	U.88892	U.95649	U.99226	U.99226	U.99226	U.99226	U.99226
O1(G)	U.33305	U.33268	U.33158	U.32817	U.31645	U.27683	U.18197	U.07410	U.01894	U.00319	U.00034	U.00002	U.00002	U.00002	U.00002	U.00002
O1H1(G)	U.00032	U.00071	U.00172	U.00460	U.01342	U.03920	U.08359	U.08949	U.05164	U.01964	U.00529	U.00098	U.00098	U.00098	U.00098	U.00098
O2(G)	U.00011	U.00028	U.00077	U.00235	U.00792	U.02634	U.06194	U.07399	U.04975	U.02311	U.00804	U.00206	U.00206	U.00206	U.00206	U.00206

ADDITIONAL PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS WERE LESS THAN .000005 FOR ALL ASSIGNED CONDITIONS

4102(G)

TABLE V. - THERMODYNAMIC FIRST DERIVATIVES FOR ESTIMATING EFFECT AT END OF A PROCESS DUE TO CHANGE AT BEGINNING OF THE PROCESS

	φ	$\left(\frac{\partial \varphi}{\partial \ln T_o}\right)_{P_o, P_o/P}$	$\left(\frac{\partial \varphi}{\partial \ln P_o}\right)_{T_o, P_o/P}$	
Isentropic process		Eq. (IV. 31)	Eq. (IV. 32)	
	$\ln T$	$(C_p)_o / C_p$	$-\frac{P_o V_o}{T_o C_p} \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}$	$-\frac{P_o V_o}{T_o C_p} \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o} + \frac{P V}{T C_p} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P$
	H	$(C_p)_o T$	$-\frac{P_o V_o T}{T_o} \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}$	$-\frac{P_o V_o T}{T_o} \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o} + P V$
	$\ln V$	$\frac{(C_p)_o}{C_p} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P$	$-\frac{P_o V_o}{T_o C_p} \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P$	$-\frac{P_o V_o}{C_p T_o} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o} + \frac{P V}{T C_p} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P + \left(\frac{\partial \ln V}{\partial \ln P}\right)_T$
Isenthalpic process		Eq. (IV. 34)	Eq. (IV. 33)	Eq. (IV. 35)
	$\ln T$	$\frac{(C_p)_o T_o}{C_p T}$	$\frac{P_o V_o}{C_p T} \left[1 - \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}\right]$	$\frac{P_o V_o}{C_p T} \left[1 - \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}\right] - \frac{P V}{T C_p} \left[1 - \frac{\partial \ln V}{\partial \ln T}\right)_P$
	S	$\frac{(C_p)_o T_o}{T}$	$\frac{P_o V_o}{T} \left[1 - \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}\right]$	$\frac{P_o V_o}{T} \left[1 - \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}\right] - \frac{P V}{T}$
	$\ln V$	$\frac{(C_p)_o T_o}{C_p T} \left(\frac{\partial \ln V}{\partial \ln T}\right)_P$	$\frac{P_o V_o}{C_p T} \left[1 - \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}\right] \left(\frac{\partial \ln V}{\partial \ln T}\right)_P$	$\frac{P_o V_o}{C_p T} \left[1 - \left(\frac{\partial \ln V_o}{\partial \ln T_o}\right)_{P_o}\right] - \frac{P V}{T} \left[1 - \frac{\partial \ln V}{\partial \ln T}\right)_P\right] + \frac{\partial \ln V}{\partial \ln P}_T$

TABLE VI. - CONTROL FACTOR AND ERROR PARAMETERS
DURING ITERATION FOR $\text{CH}_2 + 1.5 \text{O}_2$ AT
 $T = 300^\circ \text{K}$ and $P = 0.01 \text{ atm.}$

Iteration number	Control factor, λ	Species and equation number determining λ	Error parameter, ψ (eq. (IV.40))	Gibbs free energy, $G/\sum n_i M_i$, cal/g
0	-----		1.55×10^6	+1185
1	0.00959	CO_2 , (IV.38)	1.53×10^6	-757
2	.03575	CO_2 , (IV.38)	1.43×10^6	-1818
3	.30119	CO , (IV.38)	4.22×10^5	-1430
4	.59375	CH_4 , (IV.38)	6.87×10^4	-1439
5	1.0		2.41×10^1	-1510
6	1.0		4.24×10^0	-1550
7	1.0		2.46×10^0	-1605
8	1.0		4.04×10^0	-1699
9	1.0		4.70×10^0	-1874
10	1.0		4.46×10^0	-2101
11	1.0		3.72×10^0	-2308
12	1.0		3.01×10^0	-2460
13	1.0		9.21×10^{-1}	-2502
14	.00019	H_2O , (IV.39)	1.14×10^0	-2502
15	.00040	H_2O , (IV.38)	1.14×10^0	-2502
16	.00294	H_2O , (IV.38)	1.13×10^0	-2504
17	.02193	H_2O , (IV.38)	1.08×10^0	-2517
18	.17426	H_2O , (IV.38)	7.08×10^{-1}	-2614
19	1.0		8.91×10^{-4}	-2879
20	1.0		8.82×10^{-5}	-2968
21	1.0		1.38×10^{-5}	-3006
22	1.0		6.58×10^{-7}	-3012
23	1.0		7.60×10^{-8}	-3014.2
24	1.0		1.04×10^{-8}	-3014.8
25	1.0		1.54×10^{-9}	-3015.06
26	1.0		2.61×10^{-10}	-3015.14
27	1.0		9.13×10^{-11}	-3015.169
28	1.0		2.57×10^{-11}	-3015.179
29	1.0		4.09×10^{-11}	-3015.181

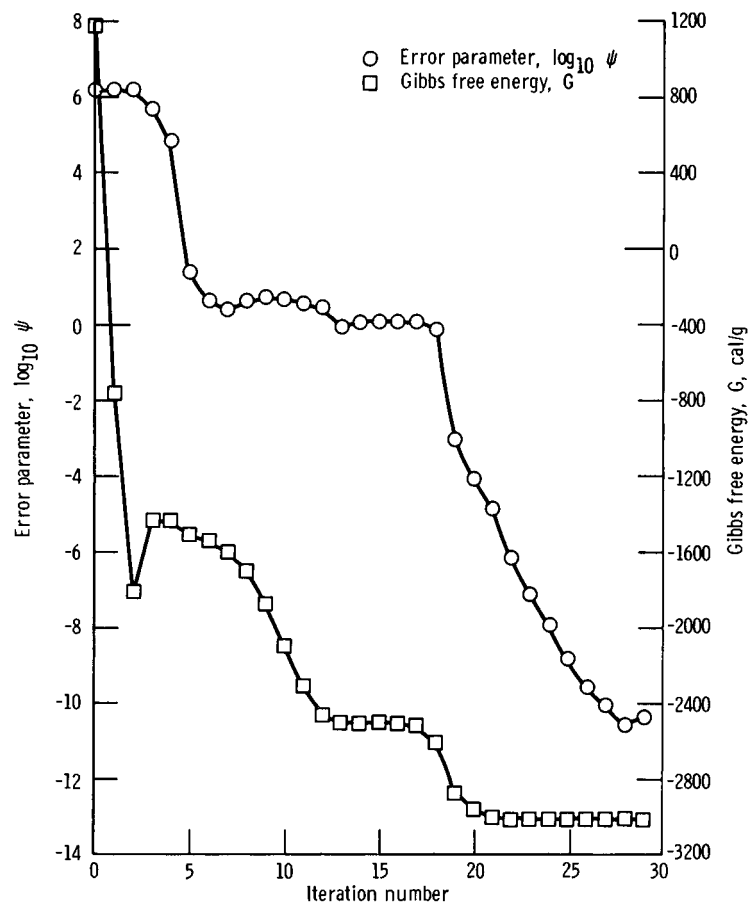


Figure 1. - Rate of convergence for $(CH_2)_x + \left(\frac{3x}{2}\right) O_2$.

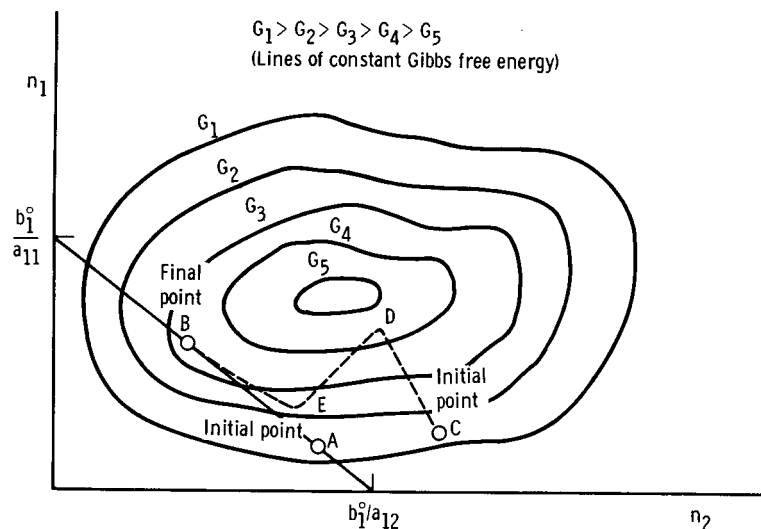


Figure 2. - Sketch of two possible paths of convergence.
Line AB ($a_{11}n_1 + a_{12}n_2 = b_1^0$): Mass constrained.
Curve CDEB: Mass unconstrained.